Studies on the Reaction Mechanism of the Photocyclization of *N*-Aryl Enamines. Dependence of Quantum Yields on Back and Side Reactions

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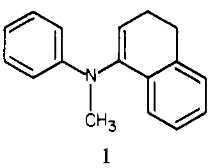
Abstract: The photocyclization of 1-(*N*-methylanilino)-3,4-dihydronaphthalene (**1**), 1-(*N*-methylanilino)-1-phenyl-1-propene (**3**), and 1-(*N*-methylanilino)-1-phenyl-1-butene (**4**) in diethyl ether and methylcyclohexane (MCH) was investigated as a function of temperature. Decay kinetics of intermediates and relative quantum yields of product and intermediate formation were measured by using flash photolysis and steady irradiation experiments. In ether only, cis–trans isomerization of the acyclic enamines (**3** and **4**) in their excited triplet states can compete with the ring-closure reaction. In methylcyclohexane, a thermal ring opening back reaction of a zwitterionic ground-state intermediate occurs which also leads to cis–trans isomerization. The kinetic constants of the back reaction are similar for enamines **3** and **4** but strikingly different for the cyclic enamine **1**, so that product quantum yields depend on temperature in an oposite manner. Qualitative molecular orbital arguments contribute to an explanation of this observation.

Introduction

The photocyclization of *N*-aryl enamines (EA) has been introduced as a useful method for the synthesis of 2,3-dihydroindoles (P), hexahydrocarbazoles, and related compounds.[1] It was shown to proceed via short-lived zwitterionic intermediates (ZW) according to Scheme I[2] in which "trivial" deactivation routes of the excited states (fluorescence, etc.) are omitted. Hereby, the excited triplet state of the zwitterion, $^{3}\mathrm{ZW}^*$, is formed in an adiabatic ring closure reaction from the triplet state of the enamine, $^{3}\mathrm{EA}^*$ (rate constant k_2). Then, after deactivation to the ground state of the zwitterion, $^{1}\mathrm{ZW}$ (k_4), hydrogen shifts take place yielding the product.[1c] Using qualitative molecular orbital symmetry arguments, Chapman et al. [1c] have reasoned that ring closure of EA in the excited state should be a conrotatory process. This conclusion is supported by recent investigations of *S*-aryl vinyl sulfides[3] which undergo an analogous photocyclization by a similar mechanism.[3b] In the latter case the analogous zwitterions were stabilized by addition to a dipolarophile, and evidence for a trans configuration of the two bridge hydrogen atoms in the addition products was obtained from their NMR signals, thus proving the conrotatory movement of the hydrogen atoms in the ring-closing step.[3a] As a consequence the trans configuration of the H atoms is retained when the products (P) are formed by suprafacial hydrogen shifts. The quantum yield of the photocyclization depends, however, on the structure of the enamine. It was found, e.g., that the quantum yield of zwitterions from ennamine **2**, in contrast to the cyclic enamine **1**, showed a strong temperature dependence while the quantum yield of the enamine triplet, $^{3}\mathrm{EA}^*$, remained constant. This was ascribed to the occurrence of a side reaction, the very fast cis–trans isomerization of the enamine double bond in the triplet state, $^{3}\mathrm{EA}^*$, having a lower activation energy than the completing ring closure. In the case of enamine **2**, of course, no discrimination between educt and product of this isomerization is possible.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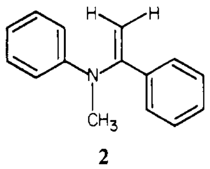
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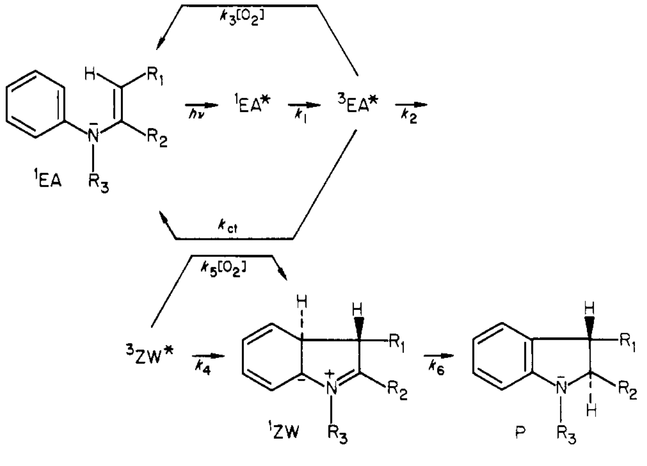
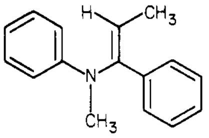
Scheme I



In the present work, therefore, the dependence of photocyclization yields on molecular structure and reaction temperature was investigated further in order to clear up mechanistic details which govern the preparative utility of enamine photocyclization. The compounds **1**, **3**, and **4** were chosen as model compounds for cyclic and acyclic enamines and exposed to flash photolysis and steady irradiation experiments. Moreover, since the reactivity of zwitterionic ground-state intermediates ($^{1}\mathrm{ZW}$) was expected to be influenced by solvent polarity, the investigations were performed in methylcyclohexane (MCH) and diethyl ether as solvents.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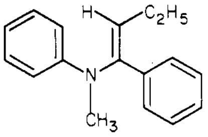
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Experimental Section

1. Preparation of Enamines. 1-(*N*-Methylanilino)-3,4-dihydronaphthalene (**1**) was prepared as described in the literature[1c,2] and showed the physical constants and spectroscopic properties reported there.

1-(*N*-Methylanilino)-1-phenyl-1-propene (3). Propiophenone (37.5 g, 0.28 mol), 15 g (0.14 mol) of *N*-methylaniline, and 7 g (0.05 mol) of

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[1] (a) Chapman, O. L.; Eian, G. L. *J. Am. Chem. Soc.* **1968**, *90*, 5329–5330. (b) Bloom, A.; Clardy, J. *Chem. Commun.* **1970**, 531–533. (c) Chapman, O. L.; Eian, G. L.; Bloom, A.; Clardy, J. *J. Am. Chem. Soc.* **1971**, *93*, 2918–2928. (d) Schultz, A. G.; Hagmann, W. K. *J. Chem. Soc., Chem. Commun.* **1976**, 726–727. (e) Nicoud, J. F.; Kagan, H. B. *Isr. J. Chem.* **1977**, *15*, 78–81. (f) Schultz, A. G.; Hagmann, W. K. *J Org. Chem.* **1978**, *43*, 3391–3393.

[2] Grellmann, K. H.; Kühnle, W.; Wolff, T. *Z. Phys. Chem.* (*Frankfurt am Main*) **1976**, *101*, 295–306.

[3] (a) Schultz, A. G.; DeTar, M. B. *J. Am. Chem. Soc.* **1976**, *98*, 3564–3572. (b) Wolff, T. *Ibid.* **1978**, *100*, 6157–6159.

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Table I. Activation Energies and Frequency Factors for the Anaerobic ZW Decay in Diethyl Ether

ZW	activation energy, kJ/mol	frequency factor, s^{-1}
5	32	7×10^5
6	16	8×10^5
7	16	8×10^5
8[a]	24	3×10^4

[a] Values taken from ref 2.

P_2O_5 were refluxed in 30 mL of toluene for 60 h in a water separator. After filtration of the mixture and evaporation of the solvent the product was distilled under vacuum and recrystallized from petroleum ether-benzene to yield 7 g (0.023, 17%) of **3**: bp 145 °C (0.2 mm); mp 56 °C; UV max (methylcyclohexane) 291, 247 nm; MS *m/e* (% intensity) 223 (30), 208 (22), 193 (14), 165 (17), 146 (100), 131 (31), 130 (20), 91 (22), 77 (30); ^{1}H NMR ($CDCl_3$) 2.0 (3 H, doublet), 3.5 (3 H, singlet), 6.4 (1 H, quartet), 7.1–7.8 ppm (10 H, multiplet). The NMR signals indicate that only one of the possible two isomers is formed.

1-(*N*-Methylanilino)-1-phenyl-1-butene (4). Butyrophenone diethyl ketal (11.5 g, 0.045 mol) and 4.8 g (0.045 mol) of *N*-methylaniline were heated for 3 h to 180 °C in the presence of trace amounts of *p*-toluenesulfonic acid while the ethanol formed was evaporated from the mixture. The residual was distilled under vacuum to yield 9.5 g (0.04 mol, 89%) of **4**: bp 133 °C (0.3 mm); UV max (methylcyclohexane) 290, 249 nm; MS m/e (% intensity) 237 (37), 170 (100), 193 (40), 160 (41), 132 (11), 131 (14), 130 (15), 104 (14), 92 (18), 77 (11); ^{1}H NMR ($CDCl_3$) 0.9 (3 H, triplet), 2.0 (2 H, quartet), 3.1 (3 H, singlet), 6.4 (1 H, triplet), 7.1–7.7 ppm (10 H, multiplet). The NMR signals indicate that only one of the possible two isomers is formed.

Boiling and melting points are uncorrected. Ultraviolet spectra were measured on a Beckman Acta M VII recording spectrophotometer, ^{1}H NMR spectra were recorded on a Varian EM 360 A spectrometer, and mass spectra were measured on a Varian MAT 112 spectrometer at 70 eV.

2. Flash Apparatus. Millisecond experiments were performed on a Model KR-1 flash photolysis apparatus (Applied Photophysics). Signals were recorded by a Datalab Model DL 905 transient recorder. Three to five single signals were averaged by a Datalab Model DL 4000 B signal analysis system.

For submicrosecond experiments the 350-nm emission of an excimer laser (Lambda Physik Model EMG 500) was used as excitation flash. A 150-W xenon lamp (Osram XBO) pulsed to 80 times its nominal output for 3 ms (Applied Photophysics Models 407 power supply and 410 pulsing unit) served as the monitoring light source, the light from which traversed a 2 × 0.3 cm cell perpendicularly to the exciting flash. Signals were recorded by a Tektronics Model 7633 storage oscilloscope. The cooling technique of Fischer[4] was applied.

3. Irradiations. Solutions of enamines **1**, **3**, and **4** were irradiated in a cylindrical 1-L irradiation vessel made from Solidex glass. A 125-W high-pressure mercury lamp (Philips HPK) was separated from the solution by two compartments, one of which was evacuated while cooling water was pumped through the other. The conditions were such that the 313-nm emission of the lamp was the efficacious wavelength. The irradiation vessel was cooled in an MGW-Lauda Model TK 80 Ultrakryostat. Irradiations were performed under nitrogen atmosphere and intensive stirring for 1–2.5 h (depending on the enamine) at each temperature. Less than 30% of the educt was converted within the irradiation times.

Irradiated solutions were analyzed by using a Varian MAT 112 mass spectrometer coupled to a gas chromatograph (Siemens Model L 350) containing capillary columns (10 m, Silicon OV 101).

4. Solutions. Flash experiments were carried out with about 10^{-4} M, steady irradiations with 10^{-3} M solutions. Diethyl ether (Merck, Uvasol) was used without further purification. Purification of methylcyclohexane has been published elsewhere as well as degassing and drying procedures.[3b]

Results

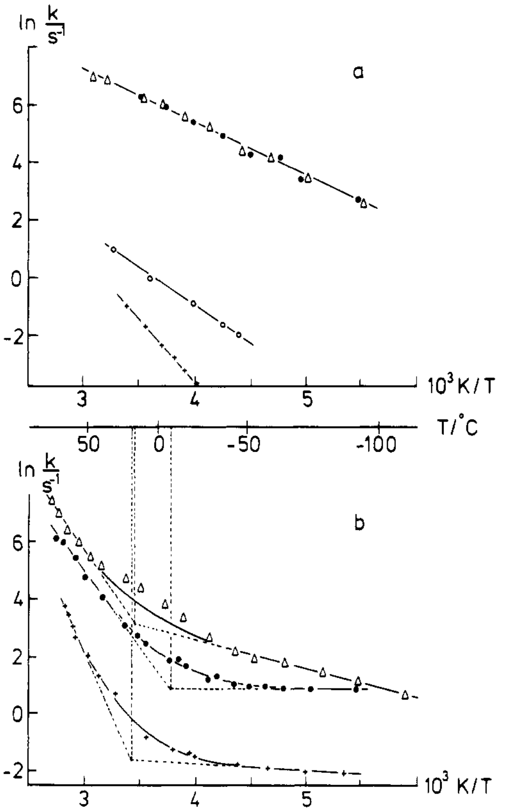
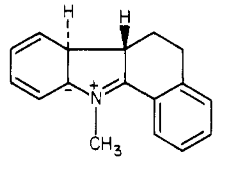


Figure 1. Temperature dependence of the anaerobic decay of zwitterions derived from enamines **1** (-+--+--+-), **2** (-o--o--o-), **3** (-●--●--●-), and **4** (-△--△--△-) in the solvents (a) diethyl ether, (b) methylcyclohexane.

Flash Experiments. In previous work[2] involving the flash photolysis of enamine **1** in diethyl ether the zwitterionic intermediate **5** had been identified already. Analogous intermediates having properties very similar to those of **5**, i.e., absorption maxima between 590 and 600 nm and lifetimes in the millisecond range at room temperature, were detected here upon flashing degassed solutions of enamines **3** and **4**. They are, therefore, assigned the zwitterionic structures **6** and **7**. Their decay was found to follow first-order kinetics under all conditions chosen in the present study.



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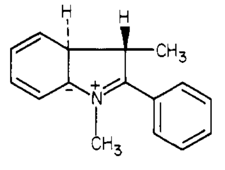

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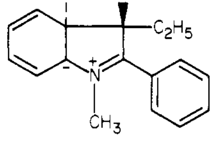

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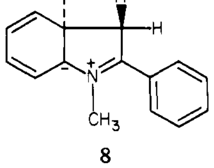
Corresponding results were also obtained when the temperature dependence of the zwitterion decay constant *k* was investigated under anaerobic conditions in diethyl ether as a solvent. Linear relations were established between ln *k* and reciprocal temperature $1/T$, as was found previously[2] for zwitterion **8**. For comparison these four relations are reproduced together in Figure 1a and evaluated in terms of activation energies and frequency factors summarized in Table I.



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In methylcyclohexane (MCH) more complicated relations between ln *k* and $1/T$ were observed (Figure 1b). Here it appears that two distinct decay channels, differing in activation energy

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(4) Fischer, E. *Mol. Photochem.* **1970**, *2*, 99–102.

Table II. Activation Energies and Frequency Factors for the Anaerobic ZW Decay in Methylcyclohexane[a]

ZW	activation energy, kJ/mol	frequency factor, s^{-1}	decay mode[b]
5	55	3×10^9	product formation
	4	1.2	ring opening
6	54	2×10^9	ring opening
	0	2.4	product formation
7	45	3×10^9	ring opening
	7	10^2	product formation

[a] Upper values for the decay mode at higher temperatures; lower values for the corresponding low-temperature decay mode. [b] See text for assignment.

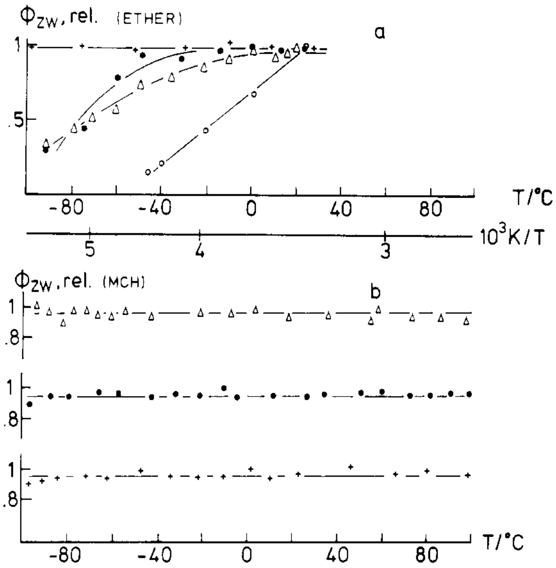
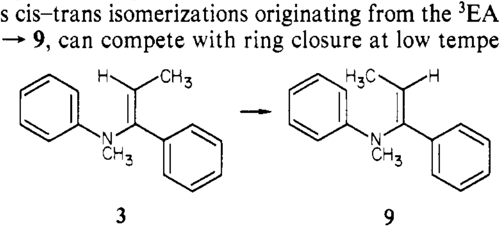


Figure 2. Relative quantum yields of zwitterions derived from enamines **1** (-+--+-), **2** (-o--o-), **3** (-●--●-), and **4** (-△--△--△-) as function of temperature (a) in ether, (b) in methylcyclohexane.

and frequency factor, exist for each zwitterion; see Table II.

Relative quantum yields for the formation of zwitterions **5**–**7** were determined by extrapolating decay curves at the wavelength of absorption maxima to zero time. These values are represented in Figure 2 as functions of temperature. In ether, no effect of temperature on the quantum yield of **5** was found as was reported before.[2] In contrast, the quantum yields of **6** and **7** decrease upon lowering the temperature. Since this effect cannot be explained by changes in absorption it is reasonable to assume that in these systems cis–trans isomerizations originating from the $^3EA^*$ state, e.g., **3** → **9**, can compete with ring closure at low temperatures



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as suggested before[2] in the case of ennamine **2**. In this latter case, however, the zwitterion quantum yield keeps rising up to room temperature, indicating that cis–trans isomerization is an important side reaction under all conditions investigated here. Isomerized educts were indeed found after steady irradiations of **3** and **4** (see below).

In MCH (Figure 2b) the quantum yields of all three zwitterions **5**–**7** were found to be independent of temperature. No indication of cis–trans isomerization in the excited triplet state was noted. In both solvents the fluorescence quantum yields were small in all cases under the conditions investigated.

More information about this temperature dependence was obtained from laser flash photolytic studies in which a solution of **3** in diethyl ether was subjected to the 350-nm emission of an excimer laser. Typical records of optical transmission vs. time are represented in Figure 3 for six different temperatures and two different wavelengths. In the plateau region (at "infinite time" on this scale) the optical density was measured as a function of wavelength and found to coincide with the absorption spectrum of zwitterion **6**, as evaluated for zero time in the millisecond experiments. Also, the temperature dependence of the optical density at 580 nm (Figure 3) agrees quite well with the curve in Figure 2a for the quantum yield of **6**. Similar experiments were carried out in MCH and led to the same result, i.e., assignment of the plateau absorption to ground-state zwitterion **6**.

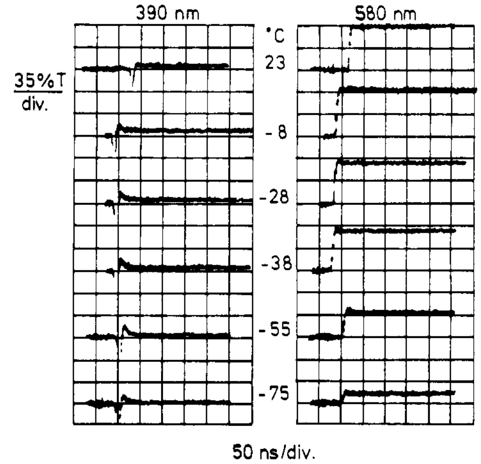


Figure 3. Optical transmission vs. time after laser flash excitation of enamine **3** in ether at two monitoring wavelengths and at six temperatures. Flash intensities vary within 10%.

Unfortunately, the spectral separation of the absorptions of $^3EA^*$, $^3ZW^*$, and ^1ZW is less than in previous experiments with **1** and **2** in ether.[2] As a consequence the building up of the ^1ZW absorption at 580 nm, which was barely resolved in the experiments[2] with **1** and **2**, could not be observed here because of the overlap of the absorption spectra of the triplet states which are formed "instantaneously" with respect to the time scale of these experiments and to the limitation in time resolution by the laser pulse width (varying from 15 to 25 ns).

In MCH no signal attributable to one of the triplet states was resolved in the wavelength and temperature range investigated (360–620 nm, +23 to −140 °C). In ether, however, where the quantum yield of zwitterion **6** drops at low temperatures (Figure 2a), Figure 3 exhibits features near zero time that must belong to another, much more rapidly decaying transient. These features are resolved best at 390 nm and at temperatures below about −30 °C. The lifetime of this transient assumes a nearly constant value of <15 ns at lower temperatures and decreases at higher temperatures (exact determinations of lifetimes and of activation energy were not possible because of overlapping laser pulse width; see above). At room temperature the absorption is hidden under the fluorescence of the probe. Therefore, with respect to quantum yield or rate constant there is no obvious interdependence of this absorption on that of zwitterion **6**. Also, no phosphorescence of the probe was detectable in the temperature region investigated. Since this precludes the transient being a direct precursor of **6**, we attribute the transient signal to absorption of the triplet state of the enamine, $^3EA^*$. This assignment agrees well with previous work[2] and confirms the above assumption that cis–trans isomerization (rotation about the double bond in $^3EA^*$) can compete with ring closure only at low temperatures and only in ether solution. Cis–trans isomerization becomes the preferred triplet decay route at low temperatures where activation energy prevents ring closure. Within the time resolution of our apparatus no signals attributable to triplet decay could be detected when a solution of **4** in ether was investigated down to temperatures approaching the melting point of ether. This indicates that ethyl substitution on the double bond increases the rate of the ring-closure reaction.

Steady Irradiations. Relative product quantum yields were determined by preparative irradiations of **1**, **3**, and **4** at different

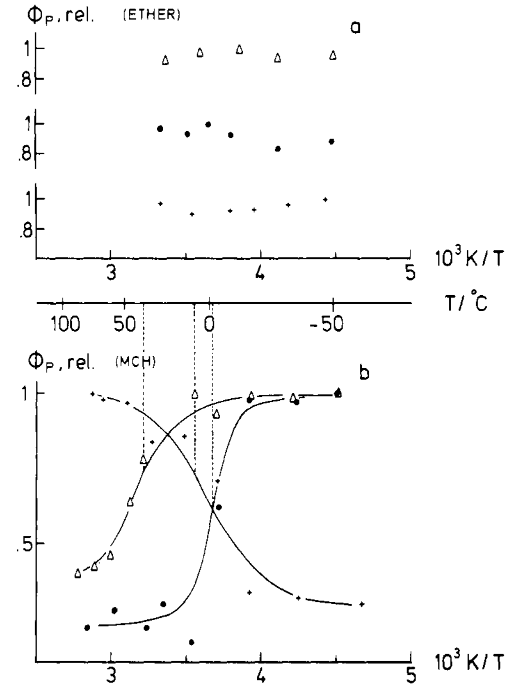
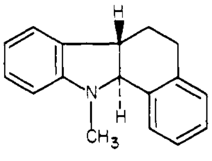


Figure 4. Temperature dependence of photoproduct yields under steady irradiation conditions, cyclization products **10** and **11** (-+--+--+-), **12** (-●--●--●-), and **13** (-Δ--Δ--Δ-): (a) in ether; (b) in methylcyclohexane.

temperatures and constant irradiation times. The reaction mixtures were analyzed using a gas chromatograph–mass spectrometer (GC–MS) combination. Irradiations of **1** in MCH or ether resulted in two photoproducts which had been previously identified by Chapman et al.[1c] as isomers **10** and **11**, **10** being formed



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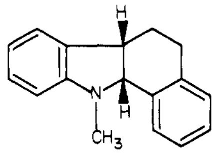

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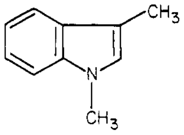
predominantly. In Figure 4 the sum of the yields of **10** and **11** in the solvents ether (Figure 4a) and MCH (Figure 4b) is plotted as a function of temperature.

GC–MS analysis of irradiated solutions of **3** and **4** showed that the cis–trans isomers of the educts and one cyclization product were present in the reaction mixtures. The cis–trans isomers had GC retention times very close to those of the educts and nearly unchanged mass spectra. The cyclized products differed from the educts in longer retention times, in fragmentation in the mass spectrometer, and in molecular masses that were two mass units lower. This was not unexpected since it was known already that 1,2,7,8-tetrahydro-*N*-methylcarbazole and 1,2-dihydro-*N*-methylcarbazole readily split off hydrogen on a gas chromatographic column.[5] The observed cyclization products are, therefore, taken to be the indoles **12** and **13** which are generated from the



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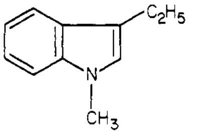

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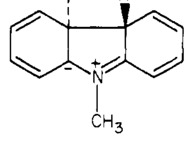
corresponding 2,3-dihydroindoles while passing through the gas chromatograph. In this way, however, information is lost with respect to the steric identity of the photoproduct **P**. Although **3** and **4** appeared to be sterically uniform educts (the structures represented by formulas **3** and **4** are the most probable ones owing to the mechanism of the preparation reaction[6]), two stereoisomeric products are expected from reirradiation of cis–trans isomerized educts (see above).

In ether (Figure 4a) quantum yields of cyclization products are seen not to vary much with temperature in the range investigated. This agrees with the temperature dependence of zwitterion yields (Figure 2), although at lower temperatures (not accessible with the apparatus used for steady irradiations) one expects a decrease of the yields of **12** and **13** due to the dropping of the corresponding zwitterion yields.

However, quite different results are obtained using MCH as a solvent (Figure 4b). Each of the three reactions exhibits a distinct temperature interval in which the quantum yield of **P** changes drastically. Within reasonable error limits the inflection points of these curves coincide with the intersections of the extrapolated lines in Figure 1b representing the temperature dependence of the zwitterion decay rate. It is evident that these two groups of phenomena are related to each other. Remembering that the zwitterion quantum yields do not depend on temperature (Figure 2b) and that no side products except cis and trans isomers of **3** and **4** are obtained, we conclude that the hydrogen migration step, i.e., the photoproduct formation from ground-state zwitterions (k_6), competes with a thermal ring opening reaction: ${}^1\mathrm{ZW} \rightarrow {}^1\mathrm{EA}$. An analogous ring opening reaction was detected by Förster et al.[7] for *N*-methyl-4a,4b-dihydrocarbazole (**14**, DHC), which is



14 (DHC)

a zwitterionic intermediate in the photoconversion of *N*-methyldiphenylamine to *N*-methylcarbazole. We are, therefore, led to assign the rate data in Table II to the decay modes listed there already. According to this interpretation the relative quantum yield vs. temperature curves in Figure 4b should approach a value of zero in the temperature range of dominating ring opening. This is very nearly the case, although some reirradiation of ring-opened molecules does seem to take place.

Discussion

A comparison of the activation energies and frequency factors listed in Table II reveals a surprising difference concerning the reactivities of zwitterions **6** and **7** on the one hand and **5** on the other. For the former two intermediates a high activation energy is required to open the ring and only a low one, belonging to an abnormally low frequency factor, to shift hydrogen in the final product-forming step (k_6). The contrary holds for the latter intermediate with the consequence that the quantum yield of **P** depends on temperature in an opposite manner (Figure 4b). An explanation of the results concerning the ring-opening step follows from qualitative molecular orbital symmetry considerations. Since (in accordance with the Woodward–Hoffmann rules)[8] the ring closure in the excited state was demonstrated to be a conrotatory process,[1,3a] it is expected that the thermal back reaction is disrotatory. However, disrotatory ring opening is possible for **6** and **7** only. Because of its cyclic structure **5** must necessarily open in a conrotatory step which must be viewed as a forbidden process showing uncommon kinetic behavior. That ring opening of **6** and **7** in MCH is indeed a disrotatory step was proven by the detection

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[5] (a) Grellmann, K. H.; Kühnle, W.; Wolff, T., to be submitted for publication. (b) Wolff, T. Ph.D. Thesis, Göttingen, 1975.

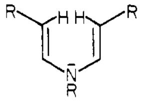
[6] (a) "Organikum", 15th ed.; VEB Deutscher Verlag der Wissenschaften: Berlin, 1976. (b) Sykes, P. "A Guide Book to Mechanism in Organic Chemistry", 2nd ed.; Longmans, Green and Co.: New York, 1965.

[7] Förster, E. W.; Grellmann, K. H.; Linschitz, H. *J. Am. Chem. Soc.* **1973**, *95*, 3108–3115.

[8] Woodward, R. R.; Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 781–859.

of cis–trans isomers of **3** and **4**. These isomers can be generated only in a ground-state back reaction of ZW since it was shown above that cis–trans isomerization in the excited triplet state ($^3EA^*$) occurred only in ether as a solvent.

One may be tempted to apply the above considerations also to the ring-opening reaction of dihydrocarbazole **14**. However, the activation energy (67 kJ/mol) and frequency factor (10^{13} s^{-1}) of this reaction do not exhibit extraordinary values.[7] Obviously, the four additional π electrons which the DHC system contains compared with ZW systems cannot be neglected in the molecular orbital considerations. It is, therefore, not possible to draw general conclusions by reducing the problem to considering a divinylamine system (**15**) which is isoelectronic with the cyclopentadienyl anion.



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Also, the other ZW decay mode, H migration (k_6), does not show the same kinetic behavior for all enamines investigated, though in ether, where hydrogen shift is the only detectable decay mode, the frequency factors are relatively close to each other (Table I). In MCH, however, the activation energies range from 55 kJ/mol in the case of **5** to practically zero in the case of **6** while the corresponding frequency factors are 10^9 and 2.4 s^{-1} (Table II). Nevertheless, extraordinary constants for k_6 were not entirely unexpected, since the analogous reaction of DHC also proceeds with zero activation energy[7] at a rate of 1.2 s^{-1}. Further peculiarities of H migration in DHC systems will be discussed in a forthcoming paper.[5]

The fact that ring opening was found only in MCH and not in ether indicates a stabilizing effect which a more polar solvent may have on zwitterionic intermediates. On the other hand, this is probably a small effect since the analogous reactions of DHC[7] are obviously independent of the polarity of the solvent. One may expect, therefore, that even in the system studied in this paper ring opening can occur in the more polar solvents whenever it is possible to extend the temperature range somewhat beyond the boiling point of ether.

A brief consideration of possible viscosity effects should perhaps be added. The changes of the quantum yields of the products appear in a temperature region (see Figure 4b) in which no dramatic changes of the viscosities of both the solvents are known so that monomolecular reactions such as ring opening and hydrogen migration will not be affected. Rather the temperature dependence of the ratio k_{ct}/k_2 (Scheme I) may be influenced by rising viscosity as the temperature approaches the melting point of ether (cf. Figure 2a). However, since an Arrhenius diagram of k_2 in the case of the cyclic enamine **1** between room temperature and −85 °C gives a straight line[5b] in ether as a solvent, a viscosity effect on k_2 is also unlikely for the reactions of the acyclic enamines **2**–**4**. Therefore, there is no obvious interdependence of rate constants and quantum yields on solvent viscosity.

Conclusions

The evidence presented here warrants the following generalizations: photocyclization yields of *N*-aryl enamines (Scheme I) depend on the molecular structure of the enamines, on temperature, and on solvent. At room temperature in nonpolar solvents high yields are expected for cyclic enamines (Scheme I, R_1 and R_2 being connected in a ring system). For acyclic enamines lower temperatures are preferable in order to suppress ring-opening back reactions. When possible, polar solvents should be used because of their stabilizing effect on the intermediate zwitterions. Irradiation of unsymmetrically substituted enamines like **3** and **4** may give mixtures of stereoisomers of the products due to reirradiation of cis–trans isomerized educts formed by back reactions.

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Use of Kinetic Isotope Effects in Mechanism Studies. Effect of an Internal Return Mechanism on the Arrhenius Behavior of Primary Hydrogen Isotope Effects[1a]

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Abstract: The effect of an internal return mechanism when the return step, k_{-1}, competes favorably with the product-forming step, k_2, on Arrhenius behavior of primary kinetic isotope effects has been modeled. The kinetic expression, $k_{obsd} = k_1k_2/(k_{-1} + k_2)$, for this situation cannot neglect either k_{-1} or k_2 and one would therefore expect to observe anomalous Arrhenius behavior. To analyze the expected temperature-dependence profile of k^H/k^D, we set $k_2^H = k_2^D$ (assuming a negligible isotope effect for the second step), replaced individual rate constants by the appropriate Arrhenius expression, and set $A_i^H = A_i^D$. Solutions of the equation allow modeling of effects and they have generated both normal and anomalous behavior. Most of the plots are linear in temperature regions normally used in kinetic studies. Of interest are solutions that predict temperature-independent isotope effects as well as Arrhenius behavior that mimics the experimental criteria for detecting quantum-mechanical tunneling.

The use of primary kinetic isotope effects in the study of organic reaction mechanisms has been well documented over the past 20 years,[2-5] and experimental techniques have improved and theory has developed to the point where the magnitude of the isotope effect has been used to describe transition-state structures. When observed effects differ from the theoretically expected maximum, it becomes increasingly important to be able to differentiate be-

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