obtained from a 1-kW Xe arc by passing through a water filter and a Barr and Stroud circular wedge filter (UGS in the UV, CGS in the visible). Its intensity as a function of wavelength was measured by an Eppley thermopile calibrated by actinometry. The measured reaction rate was corrected for the independently determined small amount of reaction due to the first beam alone.

In the determination of the lifetime of the intermediate, light from a 1-kW Xe arc was passed through a water filter, Schott WG4 and GG18 filters, and converged on the sample through an ~120° open sector in a slowly rotating large disk. The disk also contained a trigger located at an adjustable angle before the open sector. The trigger fired a Xenon Corp. water-cooled Xe flash lamp (Micropulser, 7000 V) located behind the sample. The total irradiation time was 2 h for each delay setting.

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Upper and/or Hot Excited States in Organic Photochemistry in Dense Media. A Cycloreversion in a Polycyclic Cyclobutene[†][1]

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Abstract: The mechanism of the photochemical cycloreversion reaction of the condensed cyclobutene **1** to phenanthrene in a rigid glass at 77 K with long-wavelength light involves successive absorption of two photons, with triplet **1** as the intermediate state. At short wavelengths, the reaction proceeds by the ordinary one-photon mechanism. It is concluded that thermalized S_1 and T_1 states of **1** are unreactive and that the reaction occurs with significant quantum yields in upper and/or hot singlet and triplet excited states. The results reinforce existing doubts concerning the general validity of the usual assumption of exclusive role of cool S_1 and T_1 states in organic photoreactions in dense media.

In photochemical reactions of organic molecules in fluid or rigid solutions, and even in gas phase at moderate to high pressures, it is commonly assumed without question that both internal conversion to the lowest excited electronic state of the initially reached multiplicity and thermal equilibration of vibrational motion with the surrounding medium occur much more rapidly than any chemical transformations. Mechanistic schemes proposed for reactions initiated by direct irradiation

in dense media then typically start with a thermally equilibrated ("cool") lowest excited singlet state S_1 even if the original excitation is to a higher vibronic level, or, exceptionally, with a cool lowest triplet state T_1 if the molecule contains special structural features[2] which greatly enhance the intersystem crossing rate. Similarly, mechanistic schemes for sensitized reactions typically start with a cool T_1 species. Acknowledged exceptions to the general rule that organic photochemical reactions in dense media occur only from cool S_1 and T_1 states are provided, first, by molecules in which S_2 or
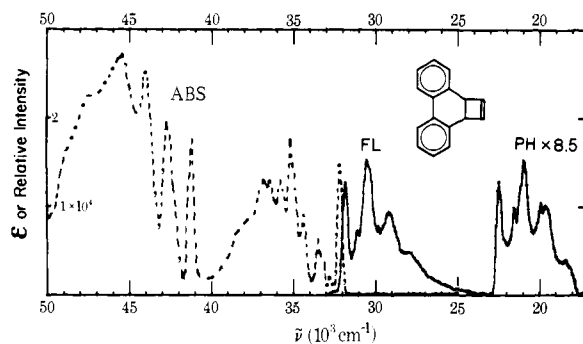
Figure 1. Absorption and uncorrected fluorescence and phosphorescence spectra of **1** in 3-MP glass at 77 K.

Figure 2. Action spectrum of the second beam in the process **1** → **2** (3-MP, 77 K). An example of the line shape of the "monochromatic" second beam is shown on the right.

T_2 are so low in energy as to be thermally populated from S_1 or T_1,[3] and second, by those in which internal conversion is exceptionally slow, as indicated by violation of Kasha's rule; e.g., azulenes[4] and thioketones.[5] Although these are very interesting cases, we shall not be concerned with them here. Rather, we shall only consider the more representative case of organic molecules for which there presently is no reason to expect exceptionally slow internal conversion among excited states.

Even for such "ordinary" cases, serious doubts concerning the general validity of the common beliefs about the exclusive role of cool S_1 and T_1 states were expressed already a decade ago (e.g., ref 6-8; our term "hot excited state reaction" is equivalent to Becker's "vibronic photochemistry"), but it turned out to be quite difficult to produce unambiguous and quantitative evidence for reactions from higher and/or hot excited states. In recent years, circumstantial and sometimes also unambiguous evidence contradicting the conventional view has been accumulating faster (for representative examples, see ref 9-15) and is becoming increasingly difficult to ignore. Some of the most convincing data are provided by investigations of biphotonic processes[10-15] of the type well known from studies of photoionization.[16] Much of the biphotonic work is concerned with processes which can be viewed as basically photophysical, and most of the reported biphotonic mechanisms of more complex reactions typical of organic photochemistry have been investigated only qualitatively. Although the results leave no doubt that organic reactions from upper and/or hot excited singlet and triplet states occur in dense media, quantitative information has been mostly limited to the dissociation of the benzylic C-X bond in aromatics.[10,14] Recently, quantum yields have been reported for the conversion of 1,2-diphenylethane into stilbene,[15] and for the electrocyclic ring opening of a polycyclic cyclobutene.[1,12] We now report quantum yields for the photocycloreversion **1** → **2** [17] which proceeds in upper and/or hot excited singlet and triplet states.

1   **2**   **3**
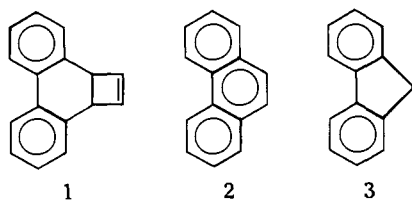
Results

Photophysics of 1. The UV absorption, fluorescence, and phosphorescence spectra of **1** resemble those of fluorene (**3**) (Figure 1). The corrected excitation spectra of both emissions follow the absorption spectrum within an uncertainty of less than 10% in the regions of strong absorption and less than 20% in the regions of weak absorption; the ratio of the intensities of fluorescence and phosphorescence is constant within ex-
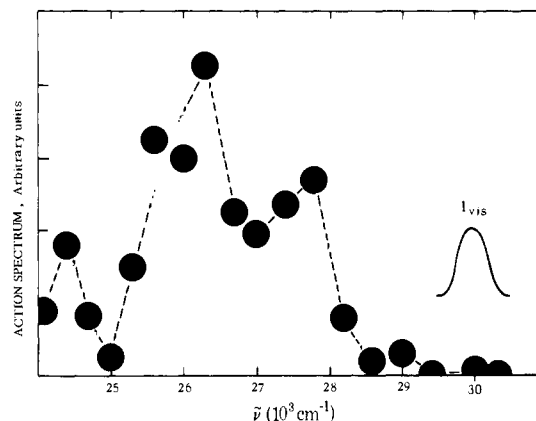
perimental error at least down to 214 nm. In 3-methylpentane (3-MP) at 77 K, ν_{0-0} (FL) = 32 000 cm^{-1}, ϕ (FL) = 0.51 ± 0.05, ν_{0-0} (PH) = 22 800 cm^{-1}, ϕ (PH) = 0.067 ± 0.01, τ (PH) = 3.45 ± 0.05 s. In a mixture of 2-methyltetrahydrofuran and 1,2-dibromoethane (74:26 by volume, 2 -MTHF-DBE) at 77 K, τ (PH) = 1.31 ± 0.05 s.

Single-Beam Photochemistry of 1. Irradiation of a rigid glass containing **1** with UV light rapidly produces phenanthrene, readily identified by its structured absorption and emission spectra. We presume that the other product is acetylene[17] but no attempt was made to prove its presence since only small amounts of **1** were available. The initial rate of disappearance of **1**, followed by UV absorption spectroscopy, is proportional to the first power of light intensity I for irradiation at 214 nm and to the second power I^2 for irradiation at 310 nm. At intermediate wavelengths (229 and 254 nm), the exponent in the light intensity dependence is nonintegral and lies between 1 and 2. The quantum yield at 214 nm was determined by uranyl oxalate actinometry as 0.012 ± 0.002.

Double-Beam Photochemistry of 1. Similarly as in ref 12, the square dependence on light intensity in the case of long-wavelength irradiation demands the presence of a relatively long-lived intermediate which absorbs the second photon, and this was confirmed by an experiment using two directly opposed beams impinging on the sample. The weak first beam (310 nm) caused only very slow reaction. The second beam was passed through a band-pass filter (330–450 nm) so as to guarantee that it was not absorbed by the ground state of **1**, and it caused no reaction in the absence of the first beam. When both beams rather than only the first beam were turned on, the reaction was accelerated by an order of magnitude. In the presence of both beams, the reaction rate was proportional to the first power of the intensity of each of the light beams separately.

The action spectrum of the second photon (Figure 2) was determined in 3-MP glass similarly as in ref 12, placing a monochromator in the second light beam. The spectrum shows some indications of fine structure and maxima in the region of the known triplet-triplet absorption spectra of biphenyl and fluorene.[18]

Further evidence for triplet **1** as the intermediate state was obtained from lifetime measurements in 3-MP and 2-MTHF-DBE solvents. First, in the presence of the intense broad-band second beam, the phosphorescence lifetime of **1** in 3-MP was shortened from 3.45 ± 0.05 to 2.8 ± 0.1 s. Second, the lifetimes of the intermediate in the two solvent systems were estimated from interrupted-beam experiments of the type described in ref 12 and compared with lifetimes of phosphorescence. A logarithmic plot of the measured rate against Δt
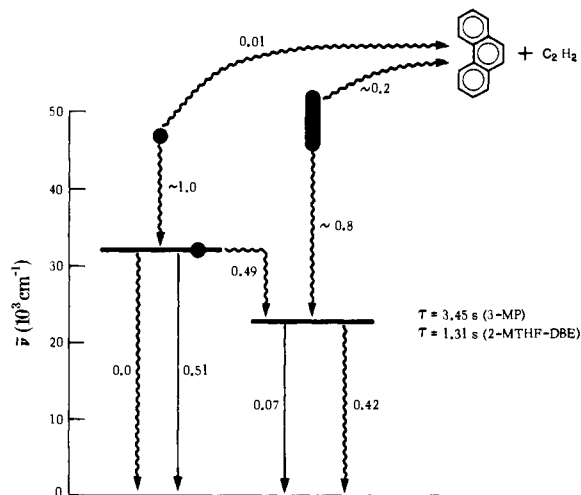
Figure 3. A summary of the photophysics and photochemistry of **1**. The numbers given are quantum yields of processes starting at levels indicated by black dots.

yielded a straight line with negative slope of 3.0 ± 0.5 s in the 3-MP solvent and of 0.9 ± 0.3 s in the 2-MTHF-DBE solvent. These values compare well with phosphorescent lifetimes and leave no doubt that triplet **1** is the sought intermediate.

Since the S_1 state of **1** is photochemically unreactive as discussed below and similar to S_1 of fluorene, we assume that for the quantum yield of intersystem crossing ϕ (isc) $= 1 - \phi$ (FL) $= 0.49$. Since the T_1 state of **1** is similar to the T_1 state of fluorene and biphenyl, we assume that its decadic molar extinction coefficient ϵ_T averaged over the region 330–450 nm is equal to 10^4 L/mol·cm (cf. the peak values of 3.5×10^4 for biphenyl and 2.1×10^4 for fluorene reported[18] for this spectral region). Using the expression of Keller and Hadley[19] for optical density in the T–T absorption region and ferrioxalate actinometry for the UV and visible beams, we obtain for the quantum yield of the second step 0.2 ± 0.1 (the quantum yield was incorrectly quoted as 0.01 in ref 1). Since our guess of the average value of ϵ_T for **1** is very crude, this is only an order of magnitude estimate.

Discussion

The spectral data indicate that the photophysical properties of **1** are unexceptional. Excitation to higher vibrational levels of S_1 or to higher excited singlet states produces thermally equilibrated S_1 state in about 100% yield. This is followed by both fluorescence and by intersystem crossing to the triplet manifold. The photochemical results show that the initial conversion to cool S_1 is not fully 100% efficient since some **2** is formed in a single-photon process upon excitation at most wavelengths, but not detectably upon excitation to the vibrationless level of S_1. Our data do not permit the determination of the smallest energy at which the singlet reaction will still proceed. This wavelength dependence of the quantum yield of the single-photon process is undoubtedly reflected in a variation of ϕ (FL) with wavelength, but even at 214 nm the reaction quantum yield is too low to detect a discrepancy between the absorption and excitation spectra with our equipment.

While there is no evidence that in cool S_1 or T_1 states **1** fragments to **2** spontaneously, the data show clearly that the T_1 state of **1** fragments with a quite substantial quantum yield upon absorption of another photon. The wavelengths efficient in this upper and/or hot excited triplet process are primarily those for which the extinction coefficient ϵ_T is large. Our data do not permit an estimate of the wavelength dependence of the efficiency of the step $T_n \rightarrow$ product and therefore do not pro-

vide a value for the minimum extra energy needed to induce the photofragmentation.

The mechanism deduced from our experimental data is presented in Figure 3. The numbers given are quantum yields of various photophysical and photochemical processes starting at the points indicated by dots. A large part of the extra energy is initially in the form of electronic energy, and it is quite likely that the photochemical reactions occur in higher electronic states. Indeed, deuterium isotope effect and quantum yield measurements of the biphotonic benzylic C–H bond photodissociation in triphenylmethane as a function of photon energy have been interpreted as implying that in this instance the reaction proceeds in an upper electronic state (predissociation).[14] It cannot be excluded, however, that in our case the actual chemical transformation is preceded by internal conversion from the initially reached higher electronic states into one of the lower states, and that the resulting vibrationally hot molecule then undergoes a chemical transformation before it loses its extra energy to the surrounding medium. This would be analogous to the recently described hot ground state reactions in thermal solution chemistry ("chemical activation").[20] In view of this uncertainty, we prefer to refer to the observed processes as "upper and/or hot" excited state reactions.

Arguments given in ref 12 for a similar set of results indicate that the singlet and triplet processes follow different pathways, i.e., that S_n and T_n do not interconvert rapidly. It is quite reasonable to postulate two distinct reaction pathways for the photofragmentation, **1** $(S_n) \rightarrow$ **2**, presumably concerted, and **1** $(T_n) \rightarrow$ **2**, presumably nonconcerted, in analogy to the various well-known singlet and triplet photocycloaddition processes which occur in the opposite direction. What makes the **1** $\rightarrow$ **2** reactions unusual is the lack of reactivity in the cool S_1 and T_1 states. This indicates the existence of barriers in the potential energy hypersurface of the S_1 and T_1 states at the geometry of **1**, which prevent the molecule from moving along bond-breaking reaction paths unless extra energy is available. It has been pointed out elsewhere[21] that the existence of a barrier in the S_1 surface of **1** follows readily from a state correlation diagram, which also suggests why no photochemical electrocyclic ring opening of the cyclobutene is observed. The barrier in the T_1 surface of **1** can be rationalized[21] but would have been harder to predict in view of the lower symmetry of the nonconcerted reaction path. It is interesting to note that the barrier in S_1 for the cycloreversion path **1** $\rightarrow$ **2** is not a result of an "abnormal orbital crossover"[21] as in cyclobutene ring opening of **1** and in similar reactions,[12,22] but appears only at the state diagram level as a result of state ordering produced by configuration interaction.[21] The same factors are likely to play a role in S_1 photochemistry of other aromatic chromophores in which S_1 corresponds to the L_b state in Platt's notation[23] and may well be responsible for the wavelength dependence observed in photochemical transformations of chromenes[6] and other aromatics.

Given that photochemical transformations are able to compete with internal conversion and/or vibrational relaxation and cooling in the singlet and triplet manifolds of **1** successfully enough to produce quantum yields of the order of several percent or even several tens of percent from higher and/or hot excited states, and given that similar numbers were measured for other bond-breaking processes,[10,12,14,15] it is only natural to wonder whether such processes are the exception or the rule. They are clearly most easily observed in molecules such as **1** in which the cool S_1 and T_1 states are unreactive, but we see no reason why they should be confined to such molecules, or even particularly favored in them. Of course, even if our suspicion that contributions from upper and/or hot excited state reactions are widespread is correct, they will only have practical impact for those processes for which the quantum yields from cool S_1 and/or T_1 are small, and this may indeed be one

of the reasons why their existence has not been generally acknowledged in organic photochemistry. Nevertheless, the usual practice of dismissing such processes out of hand appears questionable.

Upper excited state reactions with even higher quantum yields are not uncommon in inorganic photochemistry and it is interesting to ask about the origin of this dichotomy. Our guess[1] is that the difference is only apparent and is due to the fact that solution photochemists rarely work in the vacuum UV region. The d-d excitations in metalloorganic complexes and the various $\pi\pi^*$ and $n\pi^*$ excitations in organic molecules generally involve electrons which are not essential for holding the molecule together; i.e., these excited states are usually not directly dissociative. On the other hand, the more energetic charge-transfer excitations in inorganic complexes, and $\sigma \rightarrow \sigma^*$ excitations in organic compounds, typically have much more devastating effects on bonding and more easily produce dissociation before much else can happen. Many of the former occur at wavelengths longer than 200 nm, and thus are commonly encountered in inorganic solution photochemistry, while few of the latter do, so that they have largely remained hidden from organic solution photochemists.[24]

Experimental Section

A sample of purified **1** was obtained from Professor E. Vogel (University of Cologne, Germany). Naphthalene (Aldrich Chemical Co.) was zone refined; fluorene (Aldrich Chemical Co.) was gradient sublimed. All measurements were done at the temperature of liquid nitrogen in rigid 3-MP or 2-MTHF–DBE glasses. 3-MP (Phillips 66 Co.) was purified according to ref 25, and 2-MTHF (Aldrich) according to ref 26. DBE (Matheson Coleman and Bell) was shaken with concentrated sulfuric acid, then with aqueous sodium carbonate, dried with $MgSO_4$, distilled under reduced pressure of nitrogen, and stored under nitrogen over molecular sieve in a dark bottle in a freezer. EPA (American Instrument Co.) was used without further purification.

Samples were contained in 2- or 3-mm path length Suprasil cells and were degassed by freeze–pump–thaw cycles using a 10^{-6} Torr vacuum line. The cells were immersed in liquid nitrogen in a quartz Dewar vessel with Suprasil windows. Concentrations were corrected for shrinkage (a factor of 1.28 for 3-MP). All measurements were repeated independently three to five times, except for that of the lifetime of the intermediate in 2-MTHF–DBE, which was only repeated twice. The error limits given represent maximum deviations observed.

Absorption spectra were measured on a Cary 17 spectrophotometer; emission and excitation spectra were measured in the front-surface excitation mode on a homemade instrument using a variety of light sources, two Schoeffel GM-250 monochromators, and a detection system built around a S-20 response photomultiplier and a PAR 124 lock-in amplifier. The emission spectra were not corrected; the excitation spectra were corrected by comparison with absorption and excitation spectra of fluorene for which wavelength-independent ϕ (FL) was assumed. Emission quantum yields were measured with both naphthalene and fluorene as standards, with identical results. The angle between the incident and emitted beams was ~55° in order to avoid complications due to photoselection.[27] The measurements were performed as described in ref 12, using the value 0.31 for the fluorescence quantum yield and 0.033 for the phosphorescence quantum yield of naphthalene,[28] and 0.54 for the fluorescence quantum yield of fluorene[29] (the solvents used for the standards were those specified in ref 28 and 29). Lifetime measurements (λ_{exc} 310 nm, λ_{em} 473 nm in 3-MP, 308.5 and 474 nm in 2-MTHF–DBE) utilized a mechanical chopper which triggered a PDP-11/10 computer which averaged 64 decays and obtained the lifetime using a least-squares fitting procedure. The light sources and filters used were those of ref 12.

The photochemical conversion **1** → **2** was monitored as a function of time by following the disappearance of the 310-nm peak of **1**. This limited the range of useful concentrations (~10^{-4} M), but monitoring the newly appearing peaks of **2** was found to be less accurate. All conversions were kept below 15%. Because of the choice of the monitoring method for **1**, actinometry (ferrioxalate,[30] quantum yield 1.24 at 313 nm and 1.21 at 366 nm, and uranyl oxalate,[31] quantum yield

0.52 at 214 nm) generally had to be done on samples which did not absorb all of the incident light. The procedures were standard; one example will be described in detail. To determine the quantum yield of the second step, the first beam was obtained from a 200-W high-pressure Hg lamp with a water filter, Schott WG-6 filter, Balzers 310-nm interference filter, and suitable lenses and masks. A fraction of the beam was deflected into an actinometer A by reflection off a quartz plate; the rest was passed through the plate and impinged on the sample cell containing pure solvent and located in a Dewar with liquid nitrogen, and passed through the Dewar on to an actinometer B. This measurement provided a relation between light intensities at points A and B in the presence of solvent alone. Next, the Dewar was filled with room temperature water to simulate the refractive properties of liquid nitrogen and the sample cell was filled with an actinometer solution (C). This measurement provided a relation between light intensities at points A and C. Finally, the sample with **1** was placed into the Dewar filled with liquid nitrogen and actinometers at points A and B. Actinometer A now provided a measure of the light intensity incident on the sample since the ratio A:C was known from the second experiment, and actinometer B provided a measure of the light intensity absorbed by **1** present in the rigid sample by comparison with the first experiment (solvent alone). The second beam was obtained from a 1-kW Xe arc with a water filter, Schott WG-2, WG-3, and WG-4 filters, Corning CS7-39 filter, and suitable lenses and masks. A fraction of the beam was deflected into an actinometer A'; the rest was impinged onto the sample cell with actinometer solution C in a water-filled Dewar. This measurement provided a relation between light intensities at points A' and C. The actual photochemical measurement was performed with both beams on and the actinometers at positions A and A' measuring the photons delivered by each. The fraction of the second light beam absorbed by triplet **1** was too small to be measured accurately and was estimated as described in the text.

The measurement of the action spectrum was performed as in ref 12. In the determination of the lifetime of the intermediate, light from a 200-W Hg arc was filtered as above to produce the first beam (310 nm) and impinged on the sample through an open sector in a slowly rotating disk for a few seconds until the disk cut it off. After a delay Δt, another open sector in the same disk rotated into position to permit passage of a previously blocked second beam, derived as above from a filtered 1-kW Xe lamp, and kept it turned on for about 0.5 min. Then, the second beam was turned off, the first one turned on, and the cycle repeated. The delay time Δt could be selected at will by adjusting the relative position of the two open sectors on the disk. In the experiments using 2-MTHF–DBE solvent, the first beam was replaced by a filtered water-cooled Xe flashlamp similarly as in ref 12.

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Thermal Rearrangements of 1,2-Dihydropyridines

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Abstract: The *N*-(5-hexenyl)-1,2-dihydropyridine ring system (**2**) thermally rearranges to give two isomeric tricyclic imines to which the 10-methyl-9-azabicyclo[5.2.2.0$^{1.5}$]undec-8-ene structure (**5**) was assigned. The intermediacy of a 3-methyl-2-pentenyl-2,3-dihydropyridine (**8**) was detected. The thermal rearrangement of N-substituted 1,2-dihydropyridines to 3-methyl-2,3-dihydropyridines appears to be a general reaction. For example, *N*-ethyl-1,2-dihydropyridine gave the isomeric 2,3-dimethyl-2,3-dihydropyridine on heating to 200 °C. Mechanisms for these thermal rearrangements are discussed.

Authentic derivatives of the 1,2-dihydropyridine ring system without stabilizing electron-withdrawing groups on the ring are relatively rare.[1] As a consequence, little information is available concerning their chemistry. There has been recent interest[2] in these unstabilized 1,2-dihydropyridines because of their implication as pivotal intermediates in the biosynthesis of the indole alkaloids.[3]

We have recently developed a general synthesis to N-substituted 1,2-dihydropyridines[4] and now report some studies on their thermal rearrangements.

The *N*-(5-hexenyl)-1,2-dihydropyridine (**2**) is of interest because it possesses the necessary structural features to undergo an intermolecular Diels–Alder reaction[5] to give the tricyclic isoquinuclidine ring system analogous to that present in *Iboga* alkaloids. This type of synthetic methodology has been suggested from biosynthetic studies;[6] however, heating **1** in the gas phase at 250 °C for 1 h gave a 2:1 mixture of two products whose spectral data were clearly inconsistent with the tricyclic amine **3**.

These products have similar properties and are very difficult to separate. The major component can be separated from the minor component by a tedious gas chromatographic process. The high-resolution mass spectra of these two compounds indicate that they are isomeric with the dihydropyridine **2** and
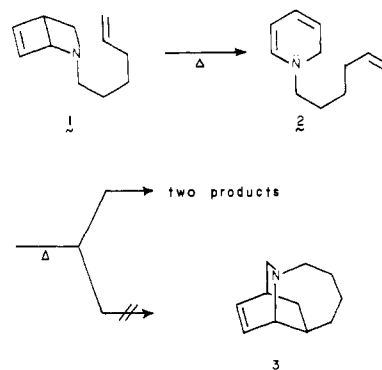
each other. Although the data suggest that they are both tricyclic, the absence of vinyl hydrogens in the ^{1}H NMR spectrum suggests that neither product is the anticipated Diels–Alder adduct **3**. Two distinguishing features of the ^{1}H NMR spectrum of the major product are a one-proton doublet at δ 8.25 and a three-proton doublet at δ 0.85. Reasonable assignments for these absorptions are an aldimine hydrogen and a methyl group adjacent to one hydrogen. The presence of the aldimine function in these products is also supported by an absorption in the infrared spectrum at 1605 cm^{-1} and by the