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Z - E PHOTOISOMERIZATION OF BENZYLIDENEBENZOCYCLOBUTENONES VIA KETENE-ALLENE INTERMEDIATES. A LASER FLASH PHOTOLYSIS STUDY.

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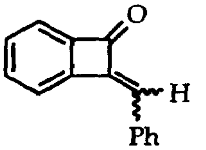
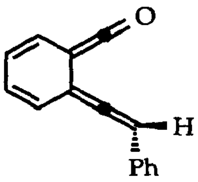
Abstract: Benzylidenebenzocyclobutenones **I-E** and **I-Z** undergo photoinduced isomerization *via* the intermediacy of ketene-allene **II** which in acetonitrile has a lifetime of ~26 μs and can be trapped with water and methanol. Trapping by the latter occurs with a rate constant of 1.2×10^4 M^{-1} s^{-1} and leads to the expected ester. In addition to Z $\rightleftharpoons$ E isomerization, product studies reveal the formation of dimeric products in very low quantum yields.

Benzocyclobutenone undergoes photoinduced ring opening readily to yield the expected vinylketene,[1] while in the case of benzocyclobutenedione the ring opening leading to the bis-ketene occurs in competition with oxacarbene-mediated reactions.[2] It was therefore of interest to examine the photochemistry of the recently prepared[3] benzylidenebenzocyclobutenones **I-E** and **I-Z**. These compounds could potentially open thermally or photochemically to the intermediate ketene-allene **II**.[4] In this study we have employed laser flash photolysis techniques to examine the formation and behavior of these intermediates and, whenever possible, we compare these results with product studies.

I-E; I-Z

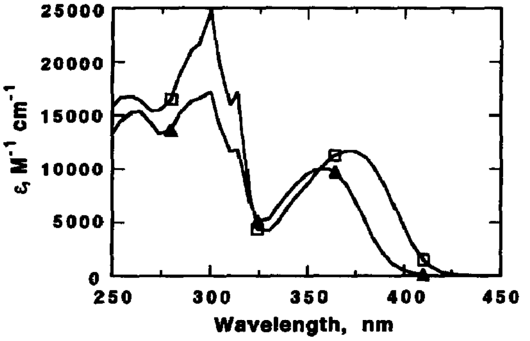


II



Results and Discussion

The UV spectra of **I-E** and **I-Z** are significantly different (see Figure 1), showing an isosbestic point at ~360 nm. Laser excitation of the E isomer in acetonitrile (typically ~0.04 M) with the 308 nm pulses from an excimer laser leads to a transient with λ_{max} ~390 nm, as shown in Figure 2. Similar experiments with the Z isomer lead to λ_{max} ~415 nm. We attribute these signals to the ketene-allene intermediate **II**. The small dependence on the precursor is not surprising, given that transient spectra reflect absorbance changes (ΔOD), rather than absolute absorbances. Thus, the bleaching of the precursors influences the spectra and shifts that from the Z-derived intermediate to longer wavelengths. The true maximum is probably close to 395 nm and is in line with those observed for related ketenes.[1,2] **I** proved to be remarkably photosensitive, and significant E $\rightleftharpoons$ Z isomerization was caused even by the analyzing beam. The problem was minimized (but not eliminated) by employing fast flow rates and limiting the monitoring beam intensity to the minimum needed for the measurements.



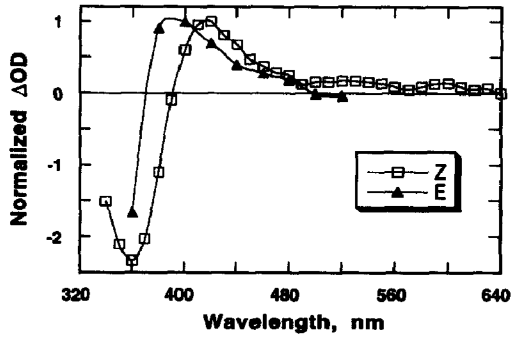


Figure 1 (left): Spectra of **I**-E (▲) and **I**-Z (□) in acetonitrile.

Figure 2 (right): Normalized transient spectra recorded following laser excitation of **I**-E and **I**-Z in acetonitrile.

The decay of **II** is dominated by cyclization to **I**-E and **I**-Z, with comparable yields. This behavior is observed independently of the precursor isomer, but is somewhat easier to monitor in the case of **I**-E, reflecting its absorption at shorter wavelengths. Figure 3 illustrates traces recorded at several key wavelengths.

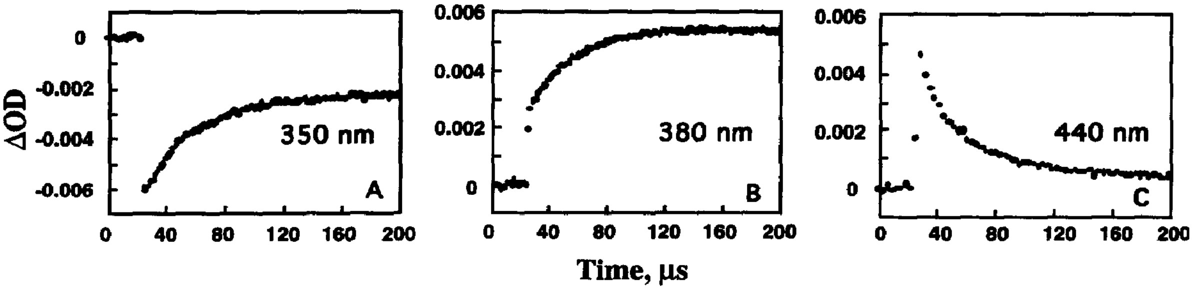


Figure 3: Transient absorbance traces recorded on 308 nm laser excitation of **I**-E in acetonitrile.

The spectra recorded after about 200 μs corresponds to a mixture of E and Z isomers and is in agreement with the permanent changes observed after the completion of steady state irradiations. Trace A was recorded at 350 nm where the extinction coefficient for **I**-E is slightly larger than for **I**-Z. About 60% recovery follows the bleaching process, although it should be noted that these percentages are influenced by any isomerization preceding the laser pulse. The remaining bleaching is probably a reflection of formation of **I**-Z, both from **II** and presumably some excited state trans-cis isomerization, along with small amounts of product formation. The main feature in trace B is the growth of **I**-Z, preceded by a step attributed to some absorption due to **II** and some excited state isomerization. Trace C was recorded in a region where **II** absorbs weakly but where **I**-E and **I**-Z show almost no overlap with the ketene-allene; thus, the signals return essentially to the pre-excitation baseline. Taken together, these results are fully consistent with the conclusion that any changes other than Z $\rightleftharpoons$ E isomerization must occur with extremely low quantum yields.

The rate constant for the cyclization process was determined from the evolution of the traces in Figure 3 and yield $k_{cycl} = 3.8 \times 10^4\ s^{-1}$, corresponding to a lifetime of 26 μs. The same lifetime was obtained using **I**-Z as the precursor for **II**.

II (from **I**-Z) was readily quenched by methanol and water. The plots were curved at low water concentration (Fig. 4, left) suggesting the involvement of two water molecules, a feature that has been widely discussed in the literature.[5-7] The plots are linear at higher concentration, and lead to apparent rate constants of 1.2×10^4 and $6.5 \times 10^3\ M^{-1}\ s^{-1}$, respectively. Similarly, using **I**-E as the precursor we measured a rate constant of $7.6 \times 10^3\ M^{-1}\ s^{-1}$ for reaction of **II** with water. Product studies in the presence of methanol reveal the formation of the expected methyl esters.[8]

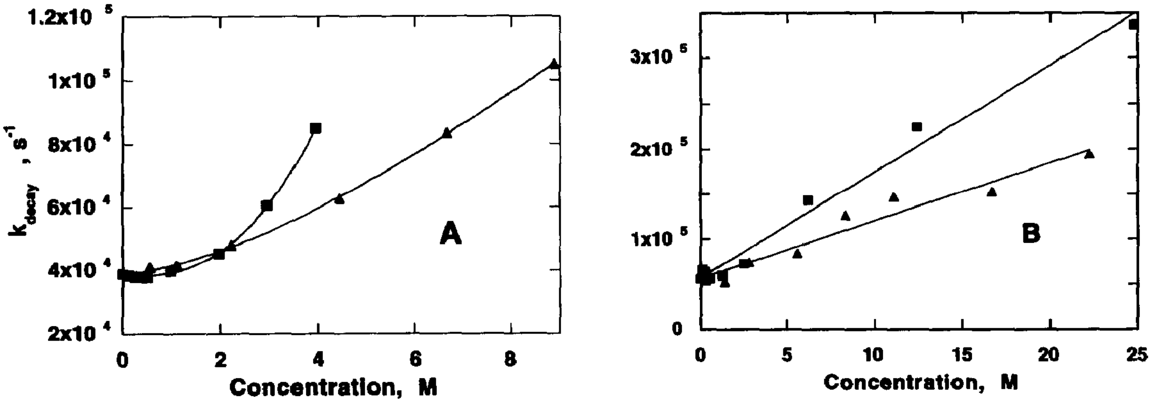
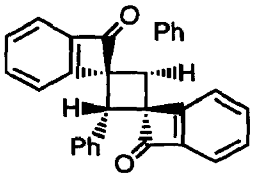


Figure 4: Quenching of **II** by water (▲) and methanol (■) in acetonitrile. Lower concentrations of water and methanol are shown in Plot A. The intercept in plot B is slightly higher than expected due to the use of static rather than flow samples. Data recorded at 410 nm.

Thus, the transient phenomena is dominated by the isomerization involving the ketene-allene **II** which can be trapped by hydroxylic scavengers. Attempts to trap it in preparative studies with maleic anhydride were unsuccessful, possibly due to the relatively short lifetime and/or a low reactivity toward such a dienophile. By comparison, the ketene from benzocyclobutenone adds to maleic anhydride with a rate constant of $1.4 \times 10^4\ M^{-1}\ s^{-1}$.[1]

Attempts to trap **II** with pyridine to form a pyridine-ylide were not conclusive. While a broadband absorption centered at ~450 nm was readily detectable in the presence of 1% pyridine in acetonitrile, we are unable to establish if these signals were formed concurrently with the decay of **II**. While we suspect that **II** is indeed the precursor, we cannot rule out possible oxacarbene intermediates.[2,7]

Product studies in relatively concentrated solutions (typically 0.1 M, irradiated at 350 nm, in methanol) reveal the formation of a dimer in preference to trapping. However, it was possible to obtain the esters almost exclusively at 254 nm, presumably due to photodecomposition of dimer to starting material at that wavelength. In these long irradiations it is irrelevant which isomer is the starting material, since a photostationary mixture is produced in the early part of the



III

photolysis. In spite of the possible formation of many dimers (head-head, head-tail, cis-trans), only **III** was formed in significant yields, and was characterized by NMR spectroscopy.[9]

Given the very low quantum yield of **III**, one cannot expect to learn about its mechanism of formation from laser experiments; however, from the observation that in preparative experiments, even in pure methanol, dimer formation exceeds ester production, we favor a mechanism for the formation of **III** involving excited states.

Finally, significant E $\rightleftharpoons$ Z isomerization probably occurs in the <10 ns time scale via the intermediacy of the excited singlet states of **I-E** and **I-Z**. In spite of this, the transient phenomena are clearly dominated by processes involving the formation and decay of the ketene-allene **II**.

Experimental

Materials: **I-E** and **I-Z** were prepared as reported earlier,[3] and purified by repeated recrystallization from hexane/ether, and the purity verified by HPLC.

Laser flash photolysis: All samples were examined under flow conditions unless otherwise indicated, and were excited with the 308 nm pulses from a Lumonics EX-510 excimer laser. The system is controlled by a Macintosh IIci computer operating with LabVIEW 2.2 software and is otherwise similar to those described elsewhere.[10] Air and nitrogen saturated samples showed identical transient behavior.

Products studies: Steady state irradiations were performed in a photoreactor equipped with nine RPR-254 or 350 nm lamps; the temperature was typically between 32-35°C. The samples were nitrogen saturated and contained in quartz tubes for 254 nm irradiation and pyrex for 350 nm irradiation. Reactions were traced by ^1H NMR.

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(8) Two esters were formed in an approximately 1:1 ratio. Key NMR data for the cis isomer are: δ 3.87 (OCH_3), 6.63 (1H, J = 12.2 Hz), and for the trans isomer δ 3.91 (OCH_3), 6.98 (1H, J = 16.3 Hz).

(9) The dimer structure was determined by a combination of ^1H NMR and ^{13}C satellite coupling, ^{13}C NMR, HETCOR, COSY, Europium shift reagent analysis and NOESY. Further details will be reported elsewhere.

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