

Short Communication

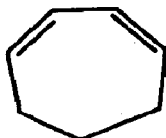
Matrix photolysis of *cis, cis*-1,3-cycloheptadiene: evidence for the existence of the highly strained *cis, trans* isomer

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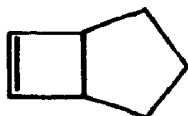
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It has been shown that either sensitized [1] or direct near-UV [2] photolysis of *cis, cis*-1,3-cyclooctadiene results in a photostationary equilibrium between the *cis, cis* and *cis, trans* isomers. Prolonged direct photolysis yields the photostable isomer bicyclo [4.2.0]oct-7-ene [2, 3]. This latter isomer is produced during sensitized photolysis only at temperatures above 80 °C as a result of thermal isomerization of the strained *cis, trans* species [1, 4]. Previous studies of *cis, cis*-1,3-cycloheptadiene (I) have demonstrated that bicyclo [3.2.0]hept-6-ene (II) is the major stable product of either direct [5 - 7] or sensitized [7, 8] photolysis of this molecule at room temperature. The results cited above for the eight-carbon analogue and the fact that cyclobutene formation from conjugated dienes is usually not a triplet state process [1] suggest that the formation of II from I by sensitized photolysis might involve the thermally unstable highly strained *cis, trans*-1,3-cycloheptadiene (III) and that III might also be produced during direct photolysis of I.



I



II



III

Although the transitory existence of III has been proposed [9] to explain the observed thermal rearrangements of isomers of I, no direct evidence of its detection has previously been published. Encouraged by recent success in the observation of other highly strained *trans* species [10 - 12] we endeavored to detect III during the low temperature photolysis of matrix-isolated I. We now wish to report our success in detecting two intermediate species by this method, both of which we believe to be conformers of III.

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Photolysis of I, isolated in an argon matrix at 20 K, using unfiltered mercury lamp radiation results in complete conversion to II over a period of about 2 h. Careful intermittent observation of the IR spectrum reveals the growth of several weak absorption maxima at 710, 780, 790, 960, 970 and 990 cm^{-1} , all of which reach maximum intensities after only a few minutes of photolysis and then slowly decrease in intensity along with the remaining I. Warming the partially photolyzed sample to 33 K for 15 min, to permit diffusion to occur, does not alter the relative intensities of any of the spectral bands. Vaporizing the partially photolyzed sample, passing the vapor through a liquid nitrogen trap, mixing the condensate with argon and redepositing at 20 K produces a spectrum in which all of the peaks associated with the intermediate product are absent and the relative intensities of I and II are the same, within experimental error, as before vaporization[†].

The maximum obtainable intensity of the weak IR peaks associated with the intermediate species can be enhanced by a factor of 2 if the photolysis is carried out with light that has passed through a bandpass filter with maximum transmittance at 251.4 nm and a half-bandwidth of 13.6 nm. Photolyzing through a Pyrex glass filter with a UV cut-off at 290 nm selectively destroys the intermediate peaks without any further photolysis of I. These results are consistent with those obtained from a UV-monitored matrix experiment which revealed a weak absorption with maxima at 285, 316 and 322 nm. These UV features reached maximum intensity after a few minutes of irradiation and then slowly disappeared. It therefore seems probable that they are due to the same intermediate species associated with the IR peaks and are responsible for the selective destruction of these peaks by radiation of wavelength greater than 290 nm.

Exposure of the partially photolyzed sample to the unfiltered light beam of our Perkin-Elmer 180 spectrophotometer results in changes in the relative intensity of the peaks attributed to the intermediate species. The 790, 990 and 970 cm^{-1} absorptions grow and the 710, 780 and 960 cm^{-1} absorptions decrease. This apparent IR photolysis occurs with a half-time of about 2 h independent of temperature from 10 to 30 K. With the IR source turned off, or the light beam blocked, no change in the relative intensity of the peaks could be observed over a period of at least 6 h at 20 K.

The only previous reports of IR photolysis of matrix-isolated molecules are the work of Pimentel and coworkers [13], which involved the Nernst glower beam induced *cis*↔*trans* isomerization of nitrous acid, and the more recent study by McNeish *et al.* [14] in which both a Nernst glower beam and an IR laser beam were found to cause $\text{Fe}(\text{CO})_4$ to react with a CH_4 matrix.

[†]The maximum absorbance reached by the bands owing to the intermediate species was less than 8% of the absorbance of the strongest bands of I and II in all of our matrix experiments. If the result of the disappearances of the intermediate is the formation of a small additional amount of II (or I), this change would have been within the limits of error of our intensity measurements.

To determine whether we could thermally induce the same change produced by IR photolysis, we deposited a neat sample of I at 20 K. Although the bands were considerably broader, we were able to observe the growth of intermediate photolysis products with absorptions at 780 and 790 cm^{-1} . The relative intensity of these bands remained constant until the temperature was raised to 60 K, at which point the 780 cm^{-1} band began to decrease and the 790 cm^{-1} band increased. At 70 K this conversion was complete in a period of several minutes. At 80 K the 790 cm^{-1} band began to decrease and at 90 K it disappeared rapidly. The much larger relative intensities of the bands due to the presence of I and II in the sample made it impossible to determine whether they increased as the 790 cm^{-1} band decreased; however, no new bands were observed.

We suggest that the above results are consistent with the identification of the intermediate species observed as two conformers of III. We propose that the less thermodynamically stable of these conformers is convertible to the more stable one by IR photolysis and that they reach a photo-stationary equilibrium with I during the first few minutes of direct low temperature photolysis. This is consistent with the known photochemistry of 1,3-cyclooctadiene [2, 3] and, if we assume that the *cis*, *trans* isomer is an intermediate in the observed formation of II from I by sensitized photolysis [7, 8], it would conform to the observation [1] that cyclobutene formation from conjugated dienes does not commonly occur by way of the triplet state.

We plan to attempt the low temperature sensitized photolysis of I, which should produce the *cis*, *trans* isomer exclusively. We also intend to examine the frequency dependence of the observed IR photolysis in an effort to understand the energy transfer involved.

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