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Demonstration of Woodward–Hoffmann Behavior in the Pulsed, Infrared Laser Induced Reaction of *cis*-3,4-Dichlorocyclobutene[1]

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Abstract: The pulsed, infrared laser induced reaction of *cis*-3,4-dichlorocyclobutene has been demonstrated to produce *cis,-trans*-1,4-dichloro-1,3-butadiene as the only detectable product even though the reaction system was not at thermal equilibrium. This is the isomer predicted by the Woodward–Hoffmann rules of conservation of orbital symmetry for a thermally allowed, ground-state, conrotatory ring opening. Even at relatively short laser pulses, reaction via a higher energy, nonallowed channel or biradical intermediate could not be made competitive within the experimental detection limit.

There is currently much interest in multiple photon infrared photochemistry which can, perhaps, be best typified as the photochemistry of the ground electronic state. Excitation with intense, pulsed, infrared laser radiation has been shown to promote molecules to high vibrational levels of the ground electronic state as a result of the absorption of many infrared photons. Much interest has centered on laser isotope separation, understanding the multiphoton absorption process, and chemical reactions induced or augmented by infrared laser radiation.[3] We have been interested in characterizing the influence of intense infrared radiation on organic systems and report in this work the effect of pulsed irradiation on *cis*-3,4-dichlorocyclobutene (**1**). Of particular concern was the behavior of this compound with respect to the Woodward–Hoffmann rules[4] concerning the conservation of orbital symmetry when induced to react in the strong field created by the megawatt infrared laser.

Experimental Section

cis-3,4-Dichlorocyclobutene (**1**) was synthesized according to well-established procedures.[5] Heating 3 Torr of **1** for 4 h at 175 °C in a 15 cm × 16 mm diameter Pyrex tube fitted with a Teflon valve and Viton O-ring produced a pure sample of *cis,trans*-1,4-dichloro-1,3-butadiene (**2**). Isomerizing **2** with a trace of I_2 at 100 °C according to the procedure of Bartlett and Wallbillich[6] produced a mixture of **2**, *cis-cis*-1,4-dichloro-1,3-butadiene (**3**), and *trans,trans*-1,4-dichloro-1,3-butadiene (**4**). The three isomers could be separated from each other and from **1** utilizing a 20 ft × 1/4 in. 10% Carbowax 20M column at 80 °C with a Varian Model 2700 gas chromatograph equipped with a flame ionization detector. The retention times of **1**, **2**, **3**, and **4** were 63.3, 24.0, 18.3, and 26.5 min, respectively. The gas chromatographic analyses of the laser reactions were complicated somewhat by small amounts of the three isomeric butadienes either in the starting material or formed during the analyses. Blank runs were conducted routinely and all laser reactions corrected accordingly. The reported results are estimated to be reliable to ±5%.

All infrared irradiations were performed with a Lumonics Model 203 CO_2 laser. The P(48) line of the 001-100 transition (916.58 cm^{-1}) was utilized to excite **1**. Mild focusing of the laser beam was accomplished with a 50-cm focal length BaF_2 lens; the sample cell was positioned at various distances between the lens and the focal point to vary the effective fluence within the cell. Several irradiations were conducted utilizing a 7.5-cm focal length BaF_2 lens which focused the laser beam within the reaction cell. Most experiments were performed using a CO_2-He-n_2 gas mix in the laser which produced a pulse shape consisting of a sharp initial spike of ~160 ns fwhm followed by a long tail of ~2500 ns (Figure 1A); removing the N_2 from the mix essentially eliminated the tail (Figure 1B). In the long pulse, approximately half the energy is contained within the initial spike and half within the tail. Pulse energies were measured with a Scientech Model 360001 power meter and temporal profiles of the pulses were determined by a photon drag detector. Samples for laser irradiation were prepared by standard vacuum line techniques and contained in 10 cm × 2.0 cm diameter Pyrex cells fitted with NaCl windows.

Results and Discussion

The use of a megawatt, pulsed, infrared laser as an energy source to drive organic chemical reactions is a recent development. Heretofore, the requisite energy to induce nonspontaneous reactions has usually been deposited in the form of either simple heat or ultraviolet-visible photons. It is not obvious that a chemical reaction initiated by the high vibrational excitation produced by an intense pulsed infrared beam will proceed in the same fashion as from simple heating which produces vibrational, rotational, and translational excitation in accordance with a Boltzmann population.

There are a number of classes of concerted organic reactions which yield totally different products and/or stereochemistry depending on whether the reactions are induced by thermal or photochemical means. The Woodward–Hoffmann rules of conservation of orbital symmetry[4] unequivocally account for these differences on the basis of symmetry properties of the ground and electronically excited states.

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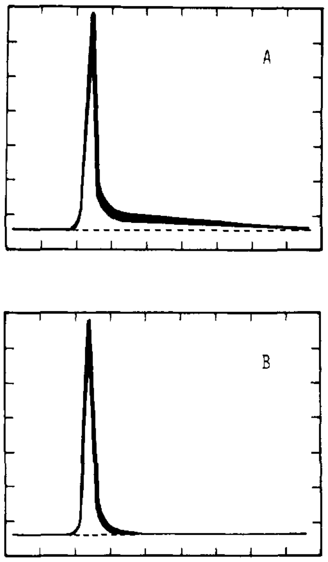


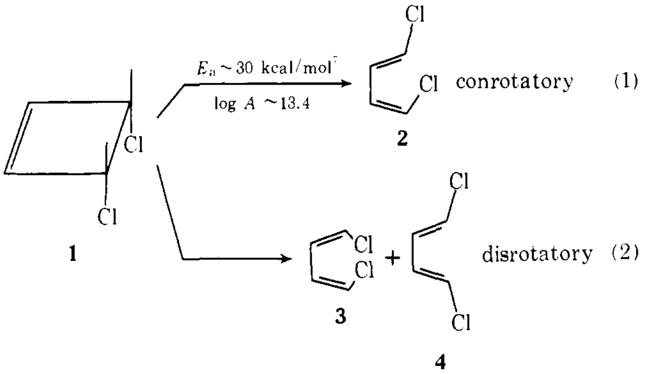
Figure 1. (A) Typical long pulse of 160 ± 20 ns initial spike followed by ~2500-ns tail (abscissa 500 ns/division; ordinate 200 mV/division). (B) Typical short pulse of 160 ± 20 nm spike and no significant tail obtained by operating laser with no N_2 in gas mix (abscissa 500 ns/division; ordinate 100 mV/division).

Table I. Pulsed Irradiation of **1** at 916.58 cm^{-1} under Various Conditions

pressure of **1**, Torr	fluence, J/cm^2	no. of pulses	pulse duration[a]	product ratio[b]
0.05	3.5	5	long	100% **2**
0.10	2.4	10	long	100% **2**
0.10	2.9	10	long	100% **2**
0.10	3.2	10	long	100% **2**
0.10	2.4	100	short	100% **2**
0.50	2.1	5	long	100% **2**
0.10	*c*	10	long	mostly **2** + unidentified peaks
2.0	*c*	10	long	mostly **2** + unidentified peaks

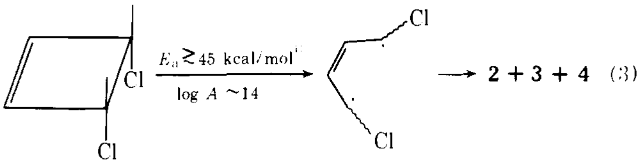
[a] Long = 160 ± 20 ns initial spike followed by ~2500-ns tail (Figure 1A); short = 160 ± 20 ns spike and no significant tail (Figure 1B). [b] Estimated accuracy ±5%. [c] Focused to point within cell.

It was the purpose of this study to subject a compound that has been demonstrated to exhibit Woodward–Hoffmann behavior to the intense field of a pulsed CO_2 laser and to determine the stereochemical outcome. The Woodward–Hoffmann rules predict that the electrocyclic ring opening of **1** should be a thermally allowed, conrotatory process to produce **2** as the only isomer. We have demonstrated adherence to this prediction; only **2** is produced upon heating **1**.



A priori, one would expect that inducement of the ring opening of **1** by the infrared laser radiation would be a ground-state reaction and that symmetry restraints would require the conrotatory process. However, the intense fields created by the pulsed CO_2 laser might nullify or lift the symmetry restraints. In addition, nearly all of the multiphoton-induced laser studies reported to date at least have assumed that reaction occurs from the ground electronic state but, very recently, collisionless infrared multiphoton production of electronically excited chromyl chloride has been reported.[10] This result was interpreted in terms of infrared transitions between high vibrational levels of the ground state and low vibrational levels of an excited electronic state lying below the ground-state dissociation limit. These observations open up the (probably remote) possibility that the infrared laser reaction of **1** occurs via the electronically excited state to produce **3** and **4** via a Woodward–Hoffmann disrotatory mechanism (reaction 2).

Of greater likelihood is that the CO_2 laser might cause **1** to react via a nonallowed alternate ground state electrocyclic pathway (e.g., eq 2) or stepwise via a biradical intermediate to produce a mixture of isomeric products (eq 3). Brauman and Archie[11] have concluded that the energies of the transition states for eq 2 and 3 are probably similar and at least 15 kcal/mol above the activation energy for the Woodward–Hoffmann allowed concerted process. It has been suggested that many more photons than are required to achieve the transition state are frequently absorbed by molecules under intense infrared radiation and a highly predissociated state of the molecule may be produced.[12-14] In our earlier work on the nonequilibrium reaction of ethyl acetate,[12] the reaction rate was found to effectively compete with V-V and V-T,R energy transfer at low pressures. RRKM theory predicted that ~45 kcal/mol in excess of the normal activation energy (48 kcal/mol) needed to be absorbed by the ester for this to occur. Richardson and Setser[13] likewise concluded that fluorinated ethane molecules acquire energy from the laser field in significant excess of the threshold energy. Similarly, Benson et al.[14] concluded from an intramolecular isotope effect study of CH_2DCH_2Cl that the average excited molecule in a pulse had an energy above reaction threshold of 33 ± 5 kcal/mol. Moreover, Brenner[15] has reported that the branching ratio for two different unimolecular reaction channels in the infrared multiphoton induced decomposition of ethyl vinyl ether can be varied by changing the laser pulse duration. With a 200-ns pulse width, the ratio of the higher energy channel (E_a = 65.0 kcal/mol, log A = 15) to the lower energy channel (E_a = 44.0 kcal/mol, log A = 11.6) was 1.46 at threshold; it was possible to cause the lower energy pathway to predominate by increasing the pulse duration. This suggests the possibility that **1** reacts via the nonallowed or biradical pathways to produce a mixture of the isomeric 1,4-dichloro-1,3-butadienes (eq 2 or 3) at short laser pulses.



Our results are summarized in Table I. Under all controlled experimental conditions investigated, only the Woodward–Hoffmann thermally allowed, ground-state isomer **2** is produced. Under strongly focused conditions, other unidentified, shorter retention time products are observed by GLC. Extensive degradation of organic compounds has been shown to occur commonly from megawatt infrared radiation under such conditions. It is important to note that the reaction system was not expected to be under thermal, Boltzmann equilibrium for the majority of these laser-induced reactions. We have demonstrated in previous work with both ethyl acetate[12] and ethanol[1a] that no significant intermolecular V–V or V–T,R transfer to thermal monitor molecules occurs at reactant pressures of 0.1 Torr or less. Therefore, it is most probable for those experiments conducted at 0.10 Torr or less that **1** is vibrationally excited by the CO_2 laser and undergoes reaction before any significant energy transfer to surrounding molecules takes place.

The experimental parameters were varied to cover the "collisionless" pressure regime (0.05–0.10 Torr) and a somewhat higher pressure (2.0 Torr) at which at least several collisions would be expected to occur during the time of the laser pulse. The fluence was varied from 2.1 J/cm^2 using mildly focusing optics to $>$100 J/cm^2 at the focal point for the last two entries in Table I. Because of the weak absorption at 916.58 cm^{-1} by **1**, some focusing was required to produce sufficient reaction product for GLC analysis. Under mild focusing conditions, **1** cleanly rearranged to **2**. Not unexpectedly, with intense focusing products other than **2**, **3**, and **4** were produced; two of the larger extraneous peaks had the same GLC retention times as *cis*- and *trans*-1,2-dichloroethylene but further attempts at identifying these products did not seem warranted. Changing the laser pulse length but keeping the total fluence constant at 2.4 J/cm^2 likewise produced only **2** within our limits of detection. A greater number of pulses was required in the short-pulse experiments to assure a sufficient quantity of product for GLC analysis; the irradiated volume was considerably reduced for these experiments since tighter focusing was required as a result of the decreased total energy output of the laser.

Our results clearly demonstrate that the megawatt infrared laser induced reaction of **1** occurs from the electronic ground state and adheres to the Woodward–Hoffmann rules. Moreover, although the laser-driven reaction is a multiphoton process which presumably[12-14] drives **1** to vibrational excitation levels considerably in excess of the normal E_a, the lowest energy reaction channel (eq 1) is followed even at short (160 ± 20 ns) laser pulses. This latter observation is in contrast to the results of Brenner[15] with ethyl vinyl ether as discussed above. Even though there are considerable similarities between the laser-induced reaction of ethyl vinyl ether and **1**, there are also distinct differences which might account for the difference in behavior. 3,4-Dichlorocyclobutene has a relatively low single photon cross section at 916.58 cm^{-1} ($\sigma = 5 \times 10^{-20}$ cm^2) which might not permit an efficient multiphoton process to drive **1** sufficiently above the E_a for reaction 1 to allow reactions 2 or 3 to become competitive. Of particular significance is the fact that the difference in A factors for the high- and low-energy channels in the present system ($\sim 10^{0.6}$) is considerably less than for ethyl vinyl ether ($10^{3.4}$). The successful inducement of the higher energy channel in Brenner's system may result as a consequence of the looser transition state (higher A factor) which leads to a rapid rise in the specific rate constant with energy above the threshold. At a sufficiently high level of vibrational excitation, the higher energy channel will actually have a larger specific rate constant than the lower energy, lower A factor channel. For the present case of *cis*-3,4-dichlorocyclobutene, the slightly higher A factors estimated for the higher energy channels (reactions 2 or 3) simply cannot compensate for the 15 kcal/mol or more difference in E_a. Therefore, it is not surprising for the present case that the only product predicted by the Woodward–Hoffmann rules was, in fact, the only observed product, particularly with the present analytical capabilities (see Experimental Section). Depending upon the rate constants for competing reaction channels, it is probable that appropriate systems exist in which an infrared laser induced reaction does not produce products in accordance with the predictions of the Woodward–Hoffmann rules even though reaction proceeds via the ground electronic state.

Acknowledgments. W.C.D. wishes to acknowledge the U.S. Department of Energy, the National Science Foundation, and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work. The majority of the pulsed laser experiments were conducted by W.C.D. while on sabbatical at the Los Alamos Scientific Laboratory and this author would like to express his appreciation to J. H. Birely, J. L. Lyman, S. M. Freund, and J. H. Clark for their hospitality and helpful discussions. D. W. Setser of Kansas State University offered valuable comments on the manuscript. D.F.K. and R.N.Z. wish to thank the National Science Foundation (Grant CHE 76-01162) for partial support of this work.

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