(7) L. Cominsky, unpublished observations.
(8) R. Kaner and I. R. Epstein, *J. Am. Chem. Soc.*, **100**, 4073 (1978).
(9) B. Chance, B. Hess, and A. Betz, *Biochem. Biophys. Res. Commun.*, **16**, 182 (1964).

Edwin J. Heilweil, Michael J. Henchman, Irving R. Epstein*
Department of Chemistry, Brandeis University
Waltham, Massachusetts 02154
Received October 30, 1978

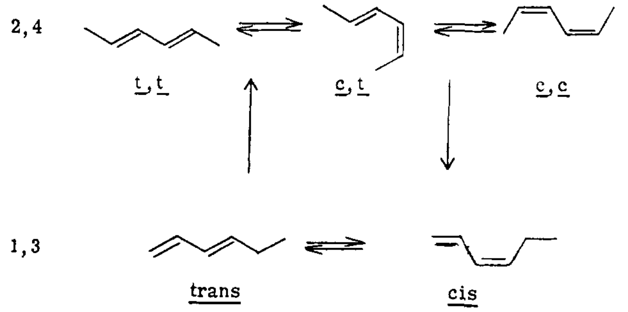
Laser-Induced Infrared Multiphoton Isomerization of Hexadienes

Sir:

It has recently been demonstrated that polyatomic molecules can undergo chemical change as the result of multiphoton absorption phenomena occurring in an intense infrared laser field.[1] Isotopic enrichment of a number of chemically and technologically important isotopes has been achieved by this technique.[2] Isotope enrichment requires the selective excitation and reaction of one component of an isotopic mixture. Frequency selective excitation of polyatomics is achievable owing to the finite vibrational normal mode frequency shifts of different isotopic compounds. Excitation is normally carried out at low pressures to avoid collision induced energy randomization among absorbing and nonabsorbing isotopic molecules. Selective excitation and reaction of structural and configurational isomers of polyatomic molecules with finite vibrational normal mode frequency shifts are also feasible.[3] Since the energy barriers for isomerization processes are frequently well below bond dissociation energies, it should be possible to effect clean, nondestructive isomerization of absorbing isomers to nonabsorbing isomers. The vibrational energy level density in the energy region required for facile isomerization is significantly lower than that in the region near the dissociation energy.[4] This intermediate excitation region is one for which very few probe techniques currently exist and is a region in which energy-transfer phenomena are not well understood. Thus isomer selective multiphoton infrared excitation offers potential both as a synthetic technique and as a probe of molecular dynamics.[5]

We report here the preliminary results of our investigation of the isomer specific infrared laser excitation and reaction of the three conformational isomers of 2,4-hexadiene (trans,trans, cis,trans, and cis,cis) and their structural isomers, the 1,3-hexadienes (trans and cis) (Scheme I). Among the significant findings of this investigation are (a) selective and nondestructive conversion of absorbing to nonabsorbing isomers, (b) preparation of isomer mixtures significantly enriched in the thermodynamically less stable isomers, and (c) the measurement of single-pulse product ratios which appear to be indicative of two or more successive isomerization processes occurring within or shortly after a single laser pulse.

Scheme I



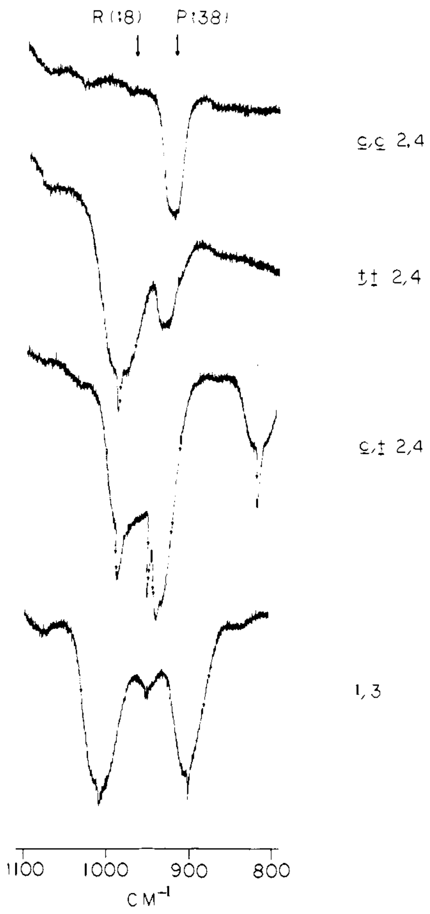


Figure 1. Infrared spectra of the hexadiene isomers in the 800-1100-cm^{-1} region. Spectra were taken at 20-Torr pressure in a 10-cm cell. Peak absorption of *cis,cis*-2,4-hexadiene is $\sim$40%; other isomers are on the same scale.

The isomeric hexadienes were obtained from Chemical Samples Corp. and used without further purification. The isomeric 2,4-hexadienes were of >98% purity as judged by analytical gas chromatography on either a dimethylsulfolane or a β,β'-oxydipropionitrile column and by GC-MS. The major impurities were the other 2,4-hexadiene isomers. 1,3-Hexadiene was a mixture of cis and trans isomers which was only partially resolved on the β,β'-oxydipropionitrile column. Infrared absorption spectra in the 800-1100-cm^{-1} region are shown in Figure 1. The most intense absorptions are attributed to modes with significant vinyl out-of-plane deformations.[6] Samples were contained in 10-cm path length by 2.5-cm i.d. Pyrex cells fitted with NaCl entrance and exit windows. High-vacuum Kontes valves were used to connect to a vacuum line or the gas inlet system of a flame ionization gas chromatograph or GC-MS. Irradiation of samples in the 10-μ to 1-Torr region was carried out via the output of a Rogowski profile double discharge CO$_2$ TEA laser. Operation on either the R(18) or P(38) transition of the 10.6-μ laser branch was confirmed using a CO$_2$ laser spectrum analyzer. Output pulses were monitored with a photon drag detector and consisted of a sharp (60 ns) spike containing $\sim$70% of the pulse energy followed by a low intensity tail of approximately 400-ns duration. An unfocused beam of $\sim$1.2-cm diameter was employed with the beam profile being monitored periodically via burn patterns on heat sensitive paper. The energy of a single pulse as measured by a calibrated thermopile was 1.6 ± 0.1 J and 0.9 ± 0.1 J on R(18) and P(38), respectively. Satisfactory GC analysis was possible for sample pressures as low as 10 μ following single-pulse irradiation.

Product ratios obtained for single-pulse excitation of the

0002-7863/79/1501-3700$01.00/0

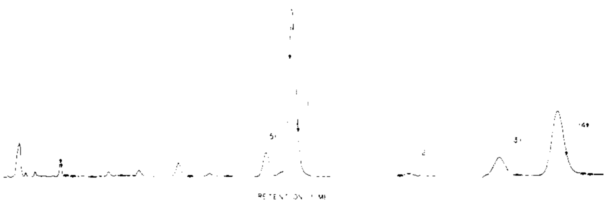


Figure 2. Gas chromatogram of *trans,trans*-2,4-hexadiene at 50-μ pressure after irradiation with 3000 pulses of the R(18) CO_2 laser transition. The unirradiated sample contained 99% *trans,trans*-2,4-hexadiene with <1% *cis,trans*-2,4-hexadiene as an impurity. (1) 1,3-hexadiene, (2) *trans,trans*-2,4-hexadiene, (3) *cis,trans*-2,4-hexadiene, (4) *cis,cis*-2,4-hexadiene, (5) cyclopentadiene.

Table I. Composition after Irradiation (Percent)[a]

parent species	1,3	*t,t*-2,4	*c,t*-2,4	*c,c*-2,4
1,3[b]	99.42	0.12	0.25	0.08
t,t-2,4[b]	0.86	97.21	1.24	0.15
c,t-2,4[b]	0.62	0.55	97.80	0.69
c,c-2,4[b]	0.00	0.00	0.00	98.69
c,c-2,4[c]	0.61	0.00	0.29	97.67

[a] Impurities present in the parent species have been subtracted out in reporting product compositions. They were 1,3-hexadiene (0.03% *t,t*-2,4, 0.06% *c,t*-2,4, 0.04% *c,c*-2,4), *trans,trans*-2,4-hexadiene (0.5% *c,t*-2,4, 0.04% *c,c*-2,4), *cis,trans*-2,4-hexadiene (0.35% *t,t*-2,4), *cis,cis*-2,4-hexadiene (0.66% 1,3, 0.03% *t,t*-2,4, 1.62% *c,t*-2,4). [b] After irradiation on the R(18) transition of the 10.6-μ laser branch. [c] After irradiation on the P(38) transition of the 10.6-μ laser branch.

isomeric hexadienes (100-μ pressure, uncorrected for irradiated volume) are given in Table I. The R(18) laser radiation is absorbed by all isomers with trans or terminal double bonds, but not by *cis,cis*-2,4-hexadiene. The absence of cis,cis isomerization upon R(18) irradiation is thus the consequence of insufficient excitation of this compound. However, *cis,cis*-2,4-hexadiene does isomerize when irradiated using the P(38) laser line. Several features of the single pulse results merit comment. Under reported conditions, excitation of cis,trans isomer produces more cis,cis isomer than the thermodynamically more stable trans,trans isomer.[7] Furthermore in all cases substantial amounts of products are formed which would be expected to require two successive isomerization processes.[8] Additionally product ratios can be made to vary as a function of fluence level and quencher pressure implying that the isomerization process occurring in this system is not a simple one. Rather it is a process which may involve multiple competitive steps. The alteration of isomeric branching ratios as a function of irradiation conditions is currently being studied via variation of power and fluence levels as well as the addition of selected quenchers. We also plan to initiate time-resolved double-resonance studies of isomeric product formation in the near future.

A gas chromatogram of the product mixture resulting from 3000-pulse R(18) irradiation of *trans,trans*-2,4-hexadiene (50 μ) is shown in Figure 2. Even though a true photostationary state is not attained, over 98% of the thermodynamically most stable hexadiene isomer has been converted into less strongly absorbing and/or less efficiently isomerizing species. This experiment again clearly indicates that *simple equilibrium thermal chemistry cannot be occurring.* Moreover the mass balance in this reaction is >85%, with the major dissociation product being cyclopentadiene. It is thus apparent that, under carefully controlled conditions, the extensive fragmentations observed in investigations of monoalkene isomerization can be avoided.[3] While product mixtures of the type shown in Figure 2 are not as of yet synthetically useful, they serve to illustrate the potential of nondestructive isomer selective laser chemistry. We are currently seeking to improve the selectivity of formation of a single hexadiene isomer (e.g., cis,cis) via simultaneous irradiation with two different laser frequencies.

Acknowledgment. We gratefully acknowledge partial support of this work by the National Science Foundation (E.W., CHE76-10333A02) and the Alfred P. Sloan Foundation (E.W. and F.D.L.). We thank Mr. Atsuo Kuki for his help in preliminary investigations of infrared photochemistry in the hexadienes.

References and Notes

(1) Ambartzumian, R. V.; Letokhov, V. S. In "Chemical and Biochemical Applications of Lasers", Moore, C. B., Ed.; Academic Press: New York, 1977; Vol. 3, Chapter 2.

(2) (a) Letokhov, V. S.; Moore, C. B. In ref 1, Vol. 3, Chapter 1. (b) Letokhov, V. S. *App. Rev. Phys. Chem.* **1977**, *28*, 133–160. (c) Cantrell, C. D.; Freund, S. M.; Lyman, J. L. In "Laser Handbook", Stich, M., Ed.; North-Holland: Amsterdam, 1978; Vol. 3. (d) Bloembergen, N.; Yablonovitch, E. *Physics Today* **1978**, May, 23–30. (e) Ambartzumian, R. V.; Letokhov, V. S. *Acc. Chem. Res.* **1977**, *10*, 61–67.

(3) (a) Glatt, I.; Yogev, A. *J. Am. Chem. Soc.* **1976**, *98*, 7087–7088. (b) Yogev, A.; Lowenstein-Benmair, R. M. J. *ibid.* **1973**, *95*, 8487–8489. (c) Ambartzumian, R. V.; Chekalin, N. V.; Dolzhikov, V. S.; Letokhov, V. S.; Lokhman, V. N. *Opt. Commun.* **1976**, *18*, 400–402. (d) Ambartzumian, R. V.; Chekalin, N. V.; Dolzhikov, V. S.; Letokhov, V. S.; Lokhman, V. N. *J. Photochem.* **1976**, *6*, 55–67.

(4) Mukamel, S.; Jortner, J. *J. Chem. Phys.* **1976**, *65*, 5204–5225.

(5) (a) Burak, I.; Quelly, T. J.; Steinfeld, J. I. *J. Chem. Phys.*, **1979**, *70*, 334–343. (b) Rice, S. A. "Internal Energy Transfer in Isolated Molecules, Ergodic and Nonergodic Behavior", to be published.

(6) Cotthup, N. B.; Daly, L. H.; Wiberley, S. E. "Introduction to Infrared and Raman Spectroscopy", Academic: New York, 1975.

(7) Doering, V. C. E.; Hauthal, H. G. *J. Prakt. Chem.* **1964**, *24*, 27–37.

(8) Frey, H. M.; Pope, B. M. *J. Chem. Soc. A* **1966**, *12*, 1701–1702.

James L. Buechele, Eric Weitz,* Frederick D. Lewis
Department of Chemistry, Northwestern University
Evanston, Illinois 60201

Received February 20, 1979

Magnetic Field Effects on the Thermolysis of Endoperoxides of Aromatic Compounds. Correlations with Singlet Oxygen Yield and Activation Entropies

Sir:

An interesting consequence of radical reactions involving singlet–triplet interconversions is the possibility of observing a variation in product distribution and/or reaction rate with the application of a steady external magnetic field, H.[1] In the absence of significant hyperfine interactions, the external field may accelerate singlet–triplet evolution in a singlet radical pair. The rate of singlet–triplet conversion is expected to increase proportionally to ΔgH (or to some power of H).[2] However, an appreciable effect of an external field is expected only if the pertinent radicals possess markedly different g factors or if extremely high external fields are involved. As an order of magnitude approximation,[3] if $\Delta g \simeq 10^{-2}$ and $H \simeq 10\,000$ G, the rate of magnetic field induced singlet–triplet conversion will approach values of $\sim 10^8$ s^{-1}. Diradical intermediates possess decay rates of this order,[4] so that a magnetic field effect on diradical reactions should be demonstrable in favorable cases. Since the products of a chemical reaction involving diradicals may depend on the presence or absence of magnetic nuclei that can interact with the diradical centers, a magnetic isotope effect[5] is also possible. We report here an investigation and demonstration of magnetic field effects on the thermolysis of endoperoxides of aromatic hydrocarbons. We show correlations of our observations with other experimental information, and we find that our results are in good qualitative agreement with theoretical predictions.

The endoperoxides studied were **1**, **2**, **3**, and **4** (Table I). In an earlier study of **1**-**4**, it was found that[6] (a) each undergoes

0002-7863/79/1501-3701$01.00/0