have been carried out in this laboratory by employing optical detection. The results of this study were unfortunately completely ambiguous: it was not possible to distinguish definitively between transient absorptions resulting from the triplet state ketone and the biradical. While NMR detection monitors only the kinetics of formation of the final diamagnetic products, at least one feature of the NMR spectrum of each product molecule is totally resolved, and assignments are readily made. It is obvious, however, that the time resolution of NMR detection will never approach that available with modern optical detection, and it is doubtful that further improvements will exceed a few tens of nanoseconds.

Acknowledgment. This research was supported by NSF Grant CHE 7821789. We are indebted to William A. Mulac of Argonne National Laboratory for his assistance in the optically detected flash photolysis experiments.

Selective Isomerization of Butadiene–Cyclobutene Systems via Infrared Multiphoton Excitation

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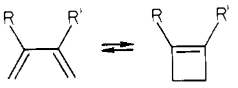
Received January 23, 1981

It is now a well-established fact that polyatomic molecules can undergo chemical change as a result of the absorption of many infrared photons from an intense laser field. By selective excitation of one isotopic compound in a mixture, it has been shown possible to preferentially dissociate that component of the mixture and thus achieve an anomalous isotope ratio in the system. This procedure has resulted in isotopic enrichment of a number of chemically and technologically important isotopes.[1] Frequency selective vibrational excitation of one isomer in a mixture of isomers is also often possible because of the finite vibrational frequency shifts that occur due to the change in energy of normal modes of different isomers.[2,3]

By selective excitation of isomers in the 2,4-hexadiene system, we have shown it possible to drive this system away from the thermodynamically most favored isomer.[3] However, in the hexadiene system, the ΔH's involved in the isomerization step were small, of the order of 1 kcal.[4] In this communication we report the achievement of efficient and selective isomerization of 2,3-dimethyl-1,3-butadiene (**1a**) and 2-methyl-1,3-butadiene (**1b**) to the cyclobutenes **2a** and **2b** (eq 1). For these species, ΔH and



1 **2** (1)

	kcal/mol	ΔS, eu
a, $R = R' = CH_3$	$+9.6$[5a,d]	-3.6[5d]
b, $R = CH_3$, $R' = H$	$+10.6$[5c,d]	-3.9[5c,d] (1.9 eu)[5d]
c, $R = R' = H$	$+11.4$[5a,b]	-3.6[5b,c]

ΔS are from ref 5a and as indicated. Where more than one reference is indicated, the appropriate values were calculated by using data from both sources. Parameters are reported for the reaction progressing left to right. This report constitutes the first example of infrared-laser-induced reactions which are substantially endoentropic and endoenthalpic.[6] By shifting irradiation frequency, the cyclobutenes can be efficiently and cleanly ring opened. The yield of cyclobutene product is highly dependent upon methyl substitution, laser fluence, and added rare gas pressure.

Table I. Isomerization Yields

parent[e]	fluence, J/cm^2	helium pressure, torr	10^6 x yield/ pulse cm^{-2}
methylbutadiene[a]	1.0	0	1.0
	2.0	0	2.9
	3.0	0	19.0
	4.0	0	35.0
	4.0	1	27.1
	4.0	2	25.6
	4.0	5	21.4
	4.0	10	17.8
methylcyclobutene[b]	2.7	0	0.85
	2.7	2	0.45
	2.7	5	0.0
	3.3	0	20.7
	3.3	5	16.0
	3.3	10	12.5
dimethylbutadiene[c]	1.7	0	2.0
	2.1	0	2.6
	2.7	0	3.5
	2.7	0.5	2.7
	2.7	1.0	1.8
	2.7	2.5	0.2
	4.7	0	140
	5.0	0	462
dimethylcyclobutene[d]	2.7	0	4.1
	3.0	0	8.0
	3.0	1.3	4.8
	3.0	5.5	3.5
	3.0	15	2.2
	3.8	0	20.0

[a] Irradiated with P(42) 10.6 μm. [b] Irradiated with P(20) 10.6 μm. [c] Irradiated with P(38) 10.6 μm. [d] Irradiated with P(22) 9.6 μm. [e] All experiments were done at a parent pressure of 100 mtorr.

Irradiation of dienes **1a–c**[7] and cyclobutenes **2a,b**[8,9] was performed by using the output of a Lumonics K203-2 TEA laser. All irradiation studies were performed in an unfocused geometry, with variations of fluence being achieved by collimation of the beam with a Gallilean telescope. For accurate definition of the beam area, beams were spatially filtered with a glass iris. Irradiation of the various isomers took place on the laser lines and over the fluence range indicated in Table I. Yields are reported as yield pulse^{-1} cm^{-2} of irradiated area. Laser energies were measured with a Scientech calorimeter and irradiation frequencies were determined with an Optical Engineering CO_2 laser spectrum analyzer. Irradiation was typically performed in a 10-cm Pyrex cell with NaCl windows. Product analysis was by gas chromatography using a 10-ft × $^1/_8$-in. column of 20% dimethylsulfolane on 80–100 mesh Chromosorb P. For each isomer system, product assignments were checked at least once via GC/MS. In the case of 1,3-butadiene (**1c**) laser irradiation produces a mixture of two unidentified isomers of mass 54, one of which is most likely cyclobutene (**2c**).

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(7) Dienes **1a**, **1b** (Aldrich Chemical Co.), and **1c** (Matheson Chemical Co.) contained <1% impurities by gas chromatographic analysis.

(8) Cyclobutenes **2a** and **2b** were prepared by the method of Srinivasan. Purification was achieved by spinning band distillation followed by preparative gas chromatography (15 ft × $^1/_4$ in.—20% dimethylsulfolane on 60–80 mesh NAW Chromosorb P). Products were identified by NMR, FTIR, and GC/MS.

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The data in Table I reveal a number of interesting features regarding these systems: (1) For the substituted butadienes, **1a** and **1b**, significant electrocyclic ring closure can be induced *even when the isomerization reaction is significantly entropically and enthalpically disfavored.* (2) Either isomer of an isomeric pair can be converted into the other isomer. (3) Isomers are produced cleanly, and yields increase significantly with increasing fluence up to $\sim$5 J/cm^2 where breakdown products begin to appear. (4) Yields decrease significantly as a function of added rare gas even at the lowest rare gas pressure used. (5) Yields increase for the substituted compounds vs. butadiene. We believe these features indicate a number of important properties about laser-induced isomerization in these systems. These will be discussed in more detail in a future publication but will be briefly considered here.

We believe that the selectivity of the isomerization process is principally due to the high contrast in absorption coefficient of the isomers at the chosen irradiation frequencies.[10] This then allows for selective "vibrational heating" of only one isomer and subsequent isomerization of that species. That this can be done even in the thermodynamically disfavored direction seemingly indicates that the deactivation rates for excited products compete with RRKM rates for the reverse isomerization reaction. Yields reported in Table I are yield/pulse cm^{-2} for samples typically irradiated for a few hundred pulses. Yields/pulse were linear as far as systematically tested which was up to a few thousand pulses. The isomerization of **1a** to **2a** was taken as far as 25% without significant decomposition and only slight diminution in the yield of product per pulse. A number of experimental studies have reported enhancement of yield and/or selectivity of a process as a function of added rare gas.[11] One postulated cause of increased yield is rotational hole filling. With **1a,b**, and for the reverse reactions we see a diminishment of yield as a function of added rare gas (see Table I). This may be due to the fact that for low fluence irradiation of a large molecule, a saturation effect like "hole burning" is not significant. Rather, rare gas deactivation may effectively compete with up pumping and/or reaction rate constants.

A recent theoretical treatment of laser-induced isomerization reactions indicates that rare gases may be used to enhance selectivity by making deactivation compete with isomer interconversion.[12] This treatment assumes that isomers interconvert rapidly on the time scale of deactivation in the absence of rare gas. Due to the low excitation conditions, the above assumption may not accurately describe isomerization in these diene systems. We are currently engaged in photoacoustic measurements and kinetic modeling to explain the substantially increased yields as a function of increasing fluence, measure actual energy deposited as a function of added rare gas, and obtain as much information as possible with regard to isomerization and quenching rates in these systems.

A variety of chemical and physical factors correlate with the degree of substitution in the butadienes. Srinivasan reported that the ultraviolet photochemical isomerization of 1,3-dienes follows roughly the same pattern as observed in laser isomerization experiments, with butadiene being the most difficult to isomerize.[9] This result was attributed to an increase with methyl substitution (**1a** > **1b** > **1c**) in the population of the ground-state s-cis conformer necessary for ring closure. Unfortunately, conformational populations are still not known with certainty. Conformational control of infrared-laser-induced ring closure would imply that ring closure is more facile than isomerization of *s-cis*-butadienes to s-trans or it is fast enough to statistically sample the s-cis and s-trans states and the density of s-cis states is greater than s-trans for the laser excited system. While either of these is possible, the first seems both entropically and energetically unlikely and an explanation may have to wait for further studies and detailed kinetic modeling of the system. Additionally a true comparison of yields should be done for equal energy deposition rather than equal fluence conditions. This is currently being worked on. It is interesting to note that the relative yields of the cyclobutenes **2a**–**c** correspond to their kinetic stabilities.[13]

Though the data we report is preliminary, taken into account with our previous work[3] and the work of others,[2] it is apparent that under appropriate conditions, clean selective isomerization can be induced in a variety of systems, even in a highly thermodynamically disfavored direction. With further study and refinement it may even be possible to use these procedures to effect the synthesis of specific isomers. In addition, we hope these systems will yield information about the dynamics of molecules in the excitation regime intermediate between the weak excitation case that usually occurs in infrared laser fluorescence studies and the higher degree of excitation necessary for dissociation. This region is one for which few experimental probes exist and is therefore not well understood with regard to energy-transfer phenomena. Thus isomer selective multiphoton excitation clearly offers potential both as a synthetic technique and as a probe of molecular dynamics.

Acknowledgment. We gratefully acknowledge support of this work by the National Science Foundation (E.W., CH79-08501) and the Alfred P. Sloan Foundation (E.W. and F.D.L.). E.W. acknowledges informative conversations with Professor Y. Haas and Professor B. Gerber.

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A Uranium–Carbon Multiple Bond. Crystal and Molecular Structure of (η^5-C_5H_5)$_3$UCHP(CH_3)$_2$(C_6H_5)

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Received December 11, 1980
Revised Manuscript Received March 23, 1981

We have recently begun an investigation of actinide–phosphoylide chemistry.[1-4] We have prepared a green complex, formulated as (η^5-C_5H_5)$_3$UCHP(CH_3)$_2$(C_6H_5) (I) on the basis of elemental analysis and spectroscopic characterization, in good yield from the reaction of (η^5-C_5H_5)$_3$UCl with an equimolar amount of Li(CH_2)(CH_2)P(CH_3)(C_6H_5). The mode of ylide–metal attachment suggested by this formulation is unusual, having been reported only for $(OC)_5MCHPR_3$ (M = Mn, Re),[5] $(CH_3)_3SiCHPR_3$,[6] and $(CH_3)_3SbCHPR_3$[7] at the time of isolation of I. This complex also differs from other uranium–phosphoylide complexes which we have structurally characterized[1-4] in that the carbon atom attached to the uranium is three- rather than four-coordinate. Since no structural data were available for compounds containing a M–CH–P unit and since the bonding between these atoms may be unusual, we have determined the crystal and molecular structure of I by X-ray diffraction. This determination not only confirms the proposed formulation of I

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