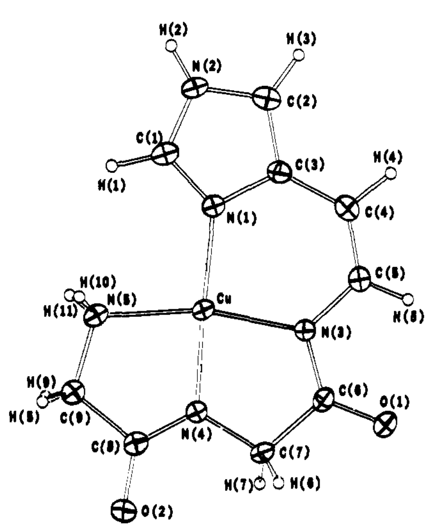

Figure 1. View of the complex of the oxidative decarboxylation product of glygly-L-his and copper(II). Hydrogen atoms are shown as spheres of arbitrary size; other thermal ellipsoids are at the 40% probability level.

dard heavy atom methods; full-matrix least-squares refinement (including all of the hydrogen atoms as fixed contributors) has now reached a conventional *R* factor of 0.038 based on 1636 independent intensities.

The structure contains the four-coordinate complex shown in Figure 1 and two water molecules. The central copper atom has approximate square planar geometry, with the four ligand nitrogen atoms bonded at normal distances[8] of 1.898 (3) to 2.028 (4) Å. The decarboxylation has occurred at atom C(5), with deprotonation at C(4) to give a formal double bond between these two atoms. The C(4)–C(5) bond length of 1.340 (6) Å is consistent with this model, and is much shorter than the values of 1.525 (6) and 1.536 (5) in [Co(L-his)(D-pen)]·H_2O and [Cu(gly-L-his-gly)]·2½H_2O, respectively;[12,13] in L-histidine, the value is 1.536 (3) Å.[14] As expected, the adjacent bonds C(3)–C(4) and C(5)–N(3) are slightly shorter than in L-histidine and these other complexes;[12-14] all other distances in the ligand are normal.

The two water molecules form hydrogen bonds to the ligand oxygen atoms O(1) and O(2), but are not involved in the copper coordination sphere. Atom O(1) forms a hydrogen bond to both water molecules, while atom O(2) forms a hydrogen bond to one water molecule and an intermolecular hydrogen bond to the imidazole nitrogen atom N(2) of an adjacent ligand.

In view of the unexpected oxidative decarboxylation, the integrity of the starting tripeptide sample was checked by amino acid analysis and found to have the correct 2:1 ratio of gly to his; thus, there is no doubt that the starting material was the tripeptide. It is noteworthy that the copper complex is very stable, and can be recrystallized from boiling water.

Oxidative decarboxylations of organic acids by metal salts (notably by lead tetraacetate in the presence of copper(II) acetate) have been described before,[15-19] but in these previous examples the product of the reaction was the stable, free olefin. The present example is the first, to our knowledge, of an oxidative decarboxylation of a peptide, and also the first in which the resulting product is tightly coordinated to the metal. The mechanism of this reaction is currently under investigation.

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Photochemistry in the Electronic Ground State. 4. Infrared Laser Induced Isomerization of Labeled Compounds. A Possible Route for Isotope Separation

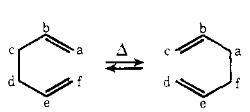
Sir:

We wish to report a quantitative isotope-selective isomerization induced by a CO_2 laser.

In previously published work performed in our laboratory, we were able to interrupt the chemical equilibrium of the cis-trans isomerization of 2-butene.[1] The partial isomerization of this reaction was accompanied by selective decomposition of the absorbing component of the reaction mixture.

Many other reports on selective reactions induced by infrared lasers dealt merely with decomposition of the absorbing species.[2]

In the present study we have investigated the reversible Cope rearrangement of 1,5-hexadiene (biallyl) labeled with deuterium at specific positions. In this system the starting material



and product are chemically identical and differ only in the position of the deuterium labeling. The reaction is defined as a [3*S*,3*S*]sigmatropic shift,[3] therefore allowed via electronic ground state. The energy of activation is 34.3 kcal mol^{-1},[4] and the secondary isotope effect is 10% per atom at room temperature in favor of deuterium at allylic positions.[5]

The experimental set-up employed in the present experiments consisted of a pulsed CO_2 TEA laser,[1] equipped with a diffraction grating. Pulse duration of about 100 ns and peak power of 0.3 MW at optimal conditions were measured by a photon-drag detector. The beam was focused by a 20 mm focal length mirror into the irradiation cell, previously described.[1]

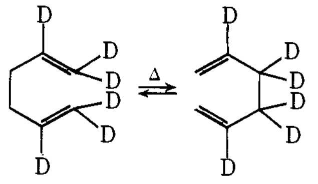
Irradiation of biallyl was performed at pressures ranging from 5 to 16 Torr. At higher pressures a breakdown, leading to acetylene formation, was observed. Irradiation products were analyzed by gas chromatography and NMR and infrared spectroscopy.

The following deuterated biallyls were investigated: 1,5-hexadiene-*1,2,5,6*-d_4 (**1**), 1,5-hexadiene-*2,3,4,5*-d_4 (**2**), 1,5-hexadiene-*1,1,2,5,6,6*-d_6 (**3**), 1,5-hexadiene-*2,3,3,4,4,5*-d_6 (**4**), 1,5-hexadiene-*1,6*-d_2 (**5**), and 1,5-hexadiene-*3,4*-d_2 (**6**).

The infrared spectrum of unlabeled biallyl possesses two absorption bands accessible to CO_2 laser excitation; a strong band centered at 10.9 μ ($\epsilon = 8.5 \times 10^{-3}$ cm^{-1} Torr^{-1}), arising from a $=CH_2$ out-of-plane bending, and a weaker band at ca. 10.1 μ due to a $=CHR$ bending.

The $=CHD$ bending of **1** and the $=CD_2$ bending of **3** are shifted to 12.5 and 14.0 μ, respectively. Therefore, CO_2 laser stimulation of the reaction is expected only in compounds **2**, **4**, and **6**, where the external vinyl sites are not labeled.

An equilibrium mixture of **3** and its rearrangement product **4** at a ratio of 0.9:1.0, respectively, was obtained by heating of **3** to 300 °C for 3 h in a sealed tube. While **4** absorbs strongly ($\epsilon = 5.8 \times 10^{-3}$ cm^{-1} Torr^{-1}) at 10.8 μ, **3** is practically transparent.



3 **4**

The mixture was irradiated at 10.8 μ at varying pressures and durations. Gas chromatographic analysis of the cell contents indicated only small amounts of volatile products in addition to the main biallyl peak.

The NMR spectrum revealed no new absorption, but a prominent increase in the ratio of integrated area of the allyl to external vinyl protons (centered at δ 2.14 and 5.0 ppm, respectively) which reflects the ratio of **3** to **4**.

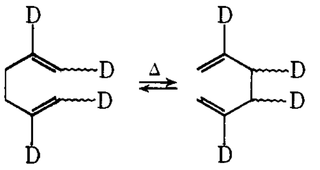
When a sample of the mixture at a pressure of 5 Torr was irradiated with 5400 pulses, the vinyl peak completely disappeared, thus indicating total consumption of **4**, leaving **3** alone.

The selectivity factor β of this system, defined by

$$\beta = ([\mathbf{3}]/[\mathbf{4}])_{\text{irradiated}}/([\mathbf{3}]/[\mathbf{4}])_{\text{initial}}$$

was greater than unity in all the irradiations performed. β was found to increase as the pressure was reduced.

A similar irradiation of **1** and its rearrangement product **2**, obtained as before, was carried out at 10.6 μ, using a totally reflecting mirror instead of a grating.



1 **2**

A selectivity factor $\beta = 3.3$ where

$$\beta = ([\mathbf{1}]/[\mathbf{2}])_{\text{irradiated}}/([\mathbf{1}]/[\mathbf{2}])_{\text{initial}}$$

was obtained after irradiation of the mixture at a pressure of 6 Torr with 5400 pulses.

To confirm our hypothesis that the observed selectivity is due to controlled rearrangement rather than decomposition of the absorbing species, irradiation of **6** under similar conditions was performed. Gas chromatographic analysis of the irradiation products showed as before only minute changes due to volatile cleavage products.

In the infrared spectrum, the appearance of a new absorption band at 12.5 μ was observed, while the band at 10.9 μ decreased to half its initial value.

To enable a quantitative treatment of the results, the irradiation products of **6** were reacted with bromine to convert biallyl to 1,2,5,6-tetrabromohexane, which was further purified by preparative TLC and recrystallization.

The NMR and infrared spectra of the tetrabromohexane were recorded and compared with those of tetrabromohexane prepared from unirradiated **6** and from independently prepared **5**. The increase in the ratio of integrated areas of the C_3-protons to C_1-protons in the NMR (centered at δ 2.2 and 3.8 ppm, respectively) after irradiation, and the behavior observed in the infrared spectrum proves unequivocally that **6** was converted to **5**. Irradiation of a sample of **6** at a pressure of 7 Torr at 10.78 μ ($\epsilon = 5.3 \times 10^{-3}$ cm^{-1} Torr^{-1}) with 3300 pulses converted 58% of **6** to **5**.

6 **5**

The maximum conversion expected, if allylic cleavage into two radicals and recombination ($E_a = 46.5$ kcal mol^{-1})[5] were the dominant reaction path, would have been 50%. The higher conversion attained proves that the main process induced by the CO_2 laser is the unimolecular, single step Cope rearrangement.

The possibility of controlling the direction of isomerization reactions, demonstrated above for a degenerate system, can, however, be applied to isotope separation purposes by choosing a nondegenerate chemical system, so that the selectively enriched component might be separated either by chemical or physical methods.

The possible use of photoisomerization for isotope separation has already been suggested by Schawlow et al.[6] However, this is the first report of an experiment demonstrating infrared laser driven isomerization sensitive to isotope labeling.

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On the Fluxional Isomerization of Cyclobutadiene

Sir:

The Woodard-Hoffmann-Longuet-Higgins-Abrahamson analysis predicts that the fluxional isomerization of cyclobutadiene is symmetry forbidden (Figure 1). However, the observed activation energy of the process is approximately 5 kcal,[1] a figure which does not suggest a forbidden process.

Various ab initio[2,3] and semiempirical[4,5] calculations are not in agreement about stabilization gained by a rectangular