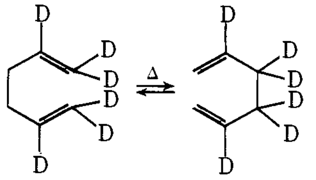
to acetylene formation, was observed. Irradiation products were analyzed by gas chromatography and NMR and infrared spectroscopy.

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**.

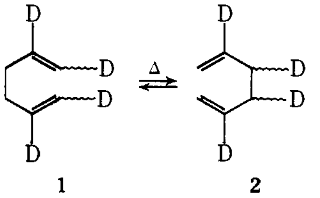
When a sample of the mixture at a pressure of 5 Torr was irradiated with 5400 pulses, the vinyl peak completely disappeared, thus indicating total consumption of **4**, leaving **3** alone.

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

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

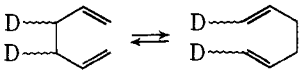
was obtained after irradiation of the mixture at a pressure of 6 Torr with 5400 pulses.

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

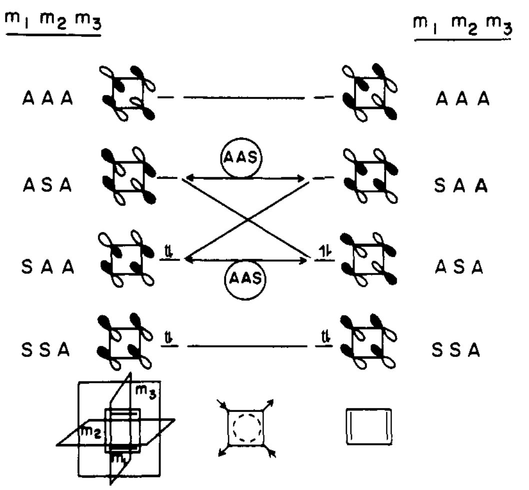


Figure 1. Correlation diagram for the fluxional isomerization of cyclobutadiene and the induced correspondences from OCAMS for an AAS distortion.

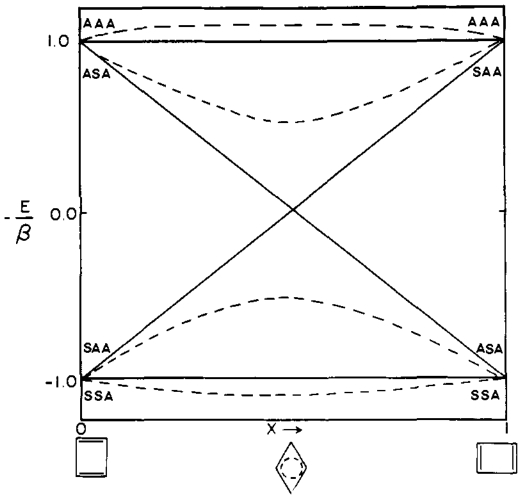


Figure 2. Hueckel orbital energy diagram. A Hamiltonian of the form $\mathbf{H} = (1 - x)\mathbf{H}(▯) + x(1 - x)y\mathbf{H}(\mathrm{AAS}) + x\mathbf{H}(▭)$ where x is the reaction coordinate and y indicates the relative amount of AAS distortion.—indicates $y = 0.0$ and - - - indicates $y = 1.0$.

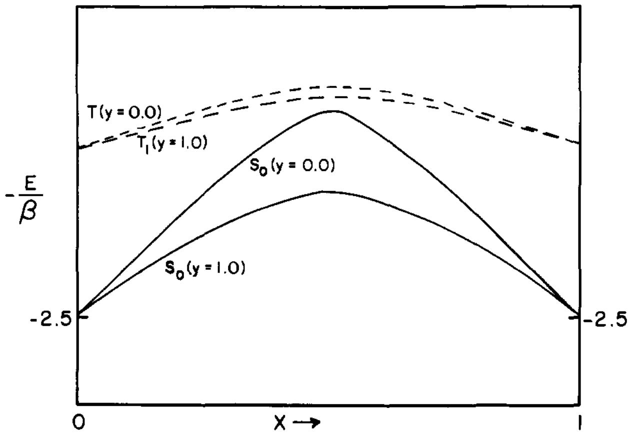


Figure 3. Hueckel-Hubbard state energy diagram for $y = 0.0$ and $y = 1.0$.

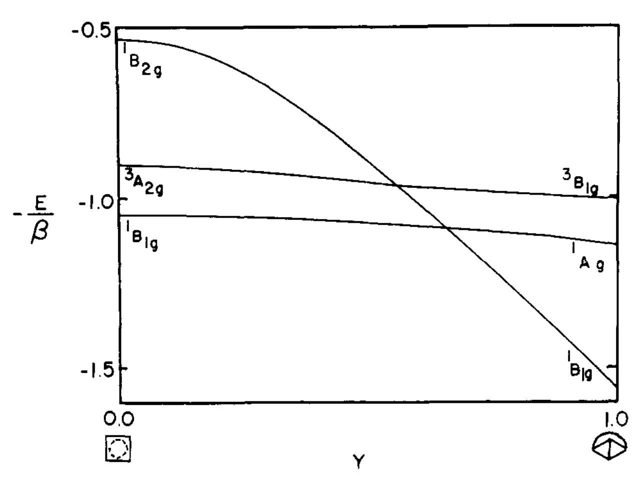


Figure 4. Low-lying Hueckel-Hubbard eigenvalues of cyclobutadiene as a function of skew-planar distortion from the square geometry.

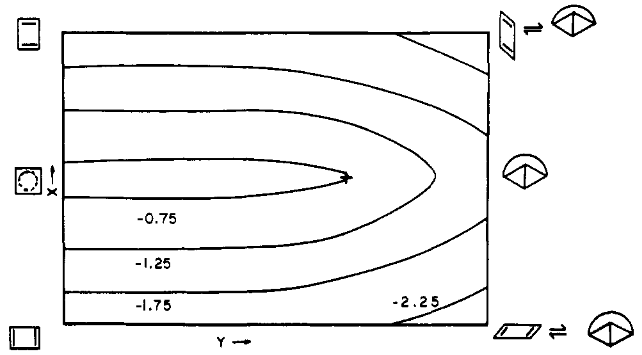
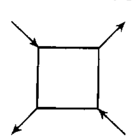


Figure 5. Schematic Hueckel-Hubbard contour plot for the fluxional isomerization of cyclobutadiene.

distortion of cyclobutadiene. The predictions range from 0.5[4] to 10.5 kcal.[2]

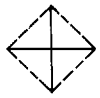
However, the ease of isomerization can be understood at the π-electronic level via an orbital correspondence analysis in maximum symmetry (OCAMS)[6] which shows that the process is allowed under a skew-planar (AAS) distortion (Figure 1) and a Hueckel-Hubbard calculation[7] is in accord with this prediction (Figure 3).

The OCAMS is schematically represented in Figure 1. The symmetries of the various orbitals are given with respect to the three mirror planes sufficient to characterize the irreducible representations of D_{2h}, the point group of rectangular cyclobutadiene. We take m_3 to be σ_h. It is seen that if one correlates orbitals of like symmetry there is an orbital crossing between HOMO and LUMO. Thus, the reaction is not likely to proceed through a square planar intermediate (an SSS distortion). However, if an AAS distortion is invoked, an SAA orbital corresponds with an ASA orbital. That is, (SAA) × (AAS) = ASA. Thus, a distortion of the type

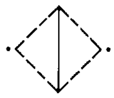


is predicted to facilitate the isomerization. This suggests a pathway for isomerization which involves a "diamond" transition state.[8]

The computed Hueckel orbital energy diagram is given in Figure 2. It is seen that for values of the distortion parameter y greater than zero the orbital crossing becomes an avoided one, in agreement with the OCAMS analysis. The Hueckel-Hubbard state energy diagram is given in Figure 3. There we find that the ground state singlet is significantly stabilized by the distortion—about an order of magnitude more than the lowest triplet. This stabilization arises as a result of a crossing of the lowest two singlet states at $y \cong 0.66$ (Figure 4). Thus, considering π-electronics only, the isomerization may have as its most favorable path one which involves distortion beyond this crossing point (Figure 5), circumventing the square intermediate. Furthermore, analysis of the ground state eigenvector indicates that the most significant structure is the singlet diradical



which is consistent with the cycloaddition reactions of 1,3-di-*tert*-butylcyclobutadiene.[9] The associated triplet diradical



is of course ruled out as the transition state in this reaction because there is little distortional stabilization in the triplet state.

Of course the inclusion of strain energy will appreciably modify the surface. It should be pointed out, however, that the π-electronic stabilization is quite large and it seems quite possible that the effects of strain energy will not completely negate the conclusions.

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The Nuclear Overhauser Enhancement of the ^{31}P Magnetic Resonance Spectrum of Inorganic Orthophosphate in Aqueous and Nonaqueous Media

Sir:

The magnitude of the nuclear Overhauser enhancement[1,2] (NOE) of the ^{31}P resonance signals of phosphates resulting from strong irradiation of protons depends on several factors present in the solvating medium, namely, the pH, the nature of the countercation, the concentration of the phosphate, the ionic strength of aqueous solutions, and whether the solvent is water, deuterium oxide, or an anhydrous organic liquid. In this communication, some data are presented to show these dependencies and to explain some of the problems we have encountered in quantitating proton-decoupled ^{31}P spectra. These findings may also explain some quantitative differences between previously published[3] ^{31}P NOE data and similar quantitative ^{31}P data being gathered in a number of different laboratories where the ^{31}P NOE was apparently not present.[4,5]

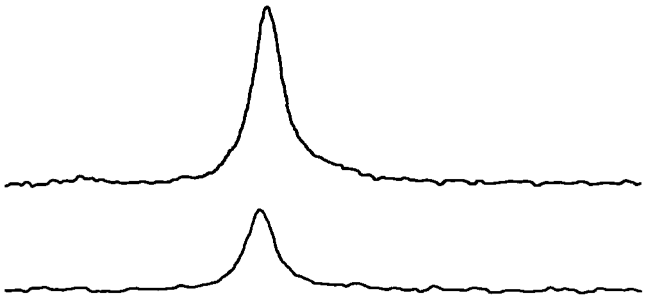

Figure 1. Comparable ^{31}P NMR spectra of tetra-*n*-hexylammonium orthophosphate (0.01 M) in 50% benzene–cyclohexane showing the nuclear Overhauser enhancement effect. The bottom spectrum is the normal ^{31}P signal obtained without irradiation of protons. The top spectrum shows the effect of strong proton irradiation; the NOE factor[2] is 2.21.

For this work, the ^{31}P spectra were obtained on a Bruker HFX-5 spectrometer[6] operating at 36.43 MHz for ^{31}P (90.00 MHz for ^{1}H) and equipped for continuous-wave and broadband, homo- and heteronuclear, ^{1}H and ^{31}P decoupling and Fourier transform[5] detection of resonances with signal averaging. Ten or thirteen millimeter spinning sample tubes were employed at a temperature of 31 °C, and the spectrometer was field-frequency stabilized through use of a 1-mm concentric capillary containing the stabilization reference, D_2O, and the phosphorus intensity reference, methylene diphosphonate (pD 9.5, sodium countercation), which shows no NOE in D_2O solution.[5] To ensure precision in the intensity measurements, 16K data point spectra were gathered employing a sweep width of 1250 Hz (400 μs per data point) and an 8-s cycling time. Signal widths at half height were almost always greater than 2 Hz,[7] and with triplicate measurements the NOE values could usually be determined to ±1% on the relatively concentrated (0.01 M in P) samples of this study.

Large well-formed crystals of orthophosphoric acid[8] (Matheson, Coleman and Bell) were dissolved in deionized water and neutralized with the appropriate concentrated base (10 M NaOH or concentrated tetra-*n*-butyl- or tetra-*n*-hexylammonium hydroxides) to produce the samples of this study. The sodium chloride was recrystallized from deionized water; the free acid of EDTA (ethylenediamine-tetraacetic acid) and the D_2O were commercial preparations. For aqueous solution studies, the appropriate salt of EDTA (0.001–0.1 M) was added to the samples to ensure that diminished NOE factor values were not the result of paramagnetic contributions to the ^{31}P T_1 relaxation. Such contributions were not likely with the nonaqueous systems since the theoretical[1,2,9] NOE was detected, implying that the predominant T_1 relaxation mechanism operating was dipole–dipole relaxation.

The anhydrous samples were prepared by evaporation of aqueous tetra-*n*-hexylammonium phosphate solutions at 30 °C, drying each sample by successive evaporations from acetone and benzene followed by anhydrous benzene, and finally purging the sample of benzene by evaporations from neat cyclohexane.[10] Only very dry preparations of hexylammonium phosphates are soluble to any significant degree in cyclohexane.

Figure 1 shows a typical ^{31}P NOE experiment. The sample was an equimolar mixture of the mono- and dianionic forms of the tetra-*n*-hexylammonium orthophosphates in a 50% benzene in cyclohexane solution. The top trace was obtained while strongly irradiating a broad band of the ^{1}H NMR (nuclear magnetic resonance) spectrum; the bottom trace shows the standard "proton coupled" ^{31}P spectrum. There are no changes in the spectral features of this resonance upon irra-