

Photochemistry of *s*-Cis Acyclic 1,3-Dienes

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Abstract: We have examined the photochemistry of several *s*-cis acyclic 1,3-dienes and found that they close to cyclobutenes at 15 K. Extensive investigation of (*E,E*)-1,4-dideuterio-2,3-dimethyl-1,3-butadiene (DDMB) has shown that there are two pathways to thermal double bond isomerization: the first through an intermediate cyclobutene with a barrier of 48 kcal/mol and the second through an allylmethylene biradical with a barrier of 55 kcal/mol. Examination of the photochemistry of *s*-cis-DDMB shows for the first time that the *s*-cis conformer undergoes both electrocyclic closure and double bond isomerization. An excited-state surface is postulated that combines these two photochemical events and includes a concerted nonsynchronous disrotatory closure. This surface also allows prediction of the partitioning ratio between the two photochemical events.

The photochemistry of 1,3-dienes has been extensively investigated.¹⁻³ It has been found that direct irradiation of 1,3-dienes in dilute solution at room temperature results mostly in cyclobutene formation^{4,5} and double bond isomerization.^{6,7} This chemistry appears to proceed through the first excited singlet state.^{8,9} In addition it is generally recognized that most acyclic 1,3-dienes exist as a mixture of two conformers.¹⁰ In most cases the more stable conformation is planar and *s*-trans about the central bond,¹¹ while the minor form has an *s*-cis configuration. Although much of the thermal chemistry and photochemistry of 1,3-dienes proceeds through this minor conformer, direct examination of *s*-cis chemistry has been limited because of its high energy relative to the *s*-trans isomer and the small barrier separating the *s*-cis from the *s*-trans isomer. In particular the participation of the *s*-cis conformer in the two major photochemical events has not been established. It has always been assumed that cyclobutene formation derives from the *s*-cis form though this has recently been questioned.¹² Indeed it is curious that the reported quantum yields for cyclobutene formation from 1,3-butadiene and 2,3-dimethyl-1,3-butadiene, 0.04¹³ and 0.1,¹⁴ respectively, are larger than the amount of *s*-cis form estimated to be present in solution. Interest in the photochemistry of the two conformers also derives from the intriguing possibility that double bond isomerization is accompanied by a simultaneous *s*-trans-*s*-cis isomerization. This type of "space-saving" isomerization process (the H.T.-n mechanism) has been proposed for the opsin-bound retinal in the visual system.¹⁵ To our knowledge double bond isomerization has not been discussed as occurring directly from the *s*-cis form. In addition, while the pathways of the two primary photochemical

events, isomerization and electrocyclic closure, have been the subject of many studies, no attempts to combine these events on one potential surface¹⁶ appear in the literature.

Contrary to a simple Hückel picture, which predicts an equal decrease in bond strength of both double bonds in the excited state, absorption of a photon by a 1,3-diene system leads to isomerization about only one of the double bonds. This result has prompted a great deal of speculation concerning the mode of formation and the geometry of the vibrationally relaxed *S*₁ species.^{17,18} From the observed mode of photochemical ring closure of *cis*- and *trans*-3-ethylidenecyclooctene, Dauben and Ritscher¹⁹ suggested that the relaxed singlet is best represented as an allylmethylene zwitterionic species.²⁰⁻²² This observation was critical to the development of the theoretical concept of sudden polarization by Bruckmann and Salem.²³ Calculations by these authors found a coexistence of two oppositely polarized zwitterionic forms on the *S*₁ surface. Both zwitterions were found to be formed via a barrierless pathway similar to that found in ethylene.²⁴ A second theoretical investigation of the geometrical relaxation in the excited state of butadiene with an *ab initio* calculation with large-scale CI also showed barrierless processes leading to both zwitterionic states,²⁵ but the presence or absence of this barrier to double bond rotation has not been determined experimentally.^{26,27}

The other major pathway, photochemical cyclobutene formation, has been essential to the understanding of orbital symmetry control of pericyclic reactions and to the concept of excited-state potential surfaces controlling photochemical reactions. The dichotomy of the mode of closure for thermal vs photochemical cyclobutene formation was a key element used by Woodward and Hoffmann^{28,29} in their approach to pericyclic reaction mechanisms. Van der Lugt and Oosterhoff³⁰ suggested that the presence of a

- (1) Srinivasan, R. *J. Am. Chem. Soc.* **1960**, *82*, 5063.
- (2) Srinivasan, R. *Adv. Photochem.* **1966**, *4*, 113-142.
- (3) Saltiel, J.; D'Agostino, J.; Megarity, E. D.; Metts, L.; Neuberger, K. R.; Wrighton, M.; Zarfiriou, O. C. *Org. Photochem.* **1973**, *3*, 1-113.
- (4) Srinivasan, R. *J. Am. Chem. Soc.* **1962**, *84*, 4141-4145.
- (5) Srinivasan, R.; Boue, S. *J. Am. Chem. Soc.* **1971**, *93*, 550-551.
- (6) Srinivasan, R. *J. Am. Chem. Soc.* **1968**, *90*, 4498-4499.
- (7) Vanderlinden, P.; Boue, S. *J. Chem. Soc., Chem. Commun.* **1975**, 932-933.
- (8) Srinivasan, R. *J. Am. Chem. Soc.* **1963**, *85*, 4045-4046.
- (9) Dauben, W. G.; Cargill, R. L.; Coates, R. M.; Saltiel, J. *J. Am. Chem. Soc.* **1966**, *88*, 2742-2745.
- (10) (a) Huckel, E. Z. *Phys.* **1932**, *76*, 628-648. (b) Aston, J. G.; Szasz, G.; Woolley, H. W.; Brickwedde, F. G. *J. Chem. Phys.* **1946**, *14*, 67-79.
- (11) (a) Almenningen, A.; Traetteburg, M. *Acta. Chem. Scand.* **1958**, *12*, 1221-1225. (b) Aten, C. F.; Hedberg, L.; Hedberg, K. *J. Am. Chem. Soc.* **1968**, *90*, 2463-2467.
- (12) Aoyagi, M.; Osamura, Y. *J. Am. Chem. Soc.* **1989**, *111*, 470.
- (13) Boue, S.; Rondelez, D.; Vanderlinden, P. *Excited States in Organic Chemistry and Biochemistry*; Pullman, B.; Goldblum, N., Eds.; D. Reidel: Dordrecht, Holland, 1977; p 199.
- (14) Srinivasan, R. *J. Am. Chem. Soc.* **1962**, *84*, 4141-4145.
- (15) (a) Liu, R. S. H.; Asato, A. E. *Proc. Natl. Acad. Sci. U.S.A.* **1985**, *82*, 259-263. (b) Liu, R. S. H.; Mead, D.; Asato, A. E. *J. Am. Chem. Soc.* **1985**, *107*, 6609-6614. (c) Liu, R. S. H.; Browne, D. T. *Acc. Chem. Res.* **1986**, *19*, 42-48.

- (16) Michl, J. *Top. Curr. Chem.* **1974**, *46*, 1-59.
- (17) Bigwood, M.; Boue, S. *J. Chem. Soc., Chem. Commun.* **1974**, 529-530.
- (18) Gerhartz, W.; Poshusta, R. D.; Michl, J. *J. Am. Chem. Soc.* **1977**, *99*, 4263-4271.
- (19) Dauben, W. G.; Ritscher, J. S. *J. Am. Chem. Soc.* **1970**, *92*, 2925-2926.
- (20) Boue, S.; Srinivasan, R. *J. Am. Chem. Soc.* **1970**, *92*, 3226-3227.
- (21) Bigwood, M.; Boue, S. *Tetrahedron Lett.* **1973**, 4311-4314.
- (22) Srinivasan, R.; Boue, S. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 320-321.
- (23) Bruckmann, P.; Salem, L. *J. Am. Chem. Soc.* **1976**, *98*, 5037-5038.
- (24) Bonacic-Koutecky, V.; Bruckmann, P.; Hiberty, P.; Koutecky, J.; Leforestier, C.; Salem, L. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 575-576.
- (25) Bonacic-Koutecky, V.; Persico, M.; Dohnert, D.; Sevin, A. *J. Am. Chem. Soc.* **1982**, *104*, 6900-6907.
- (26) (a) Hemley, R. J.; Dawson, J. I.; Vaida, V. *J. Chem. Phys.* **1983**, *78*, 2915. (b) Leopold, D. G.; Pendley, R. D.; Roebber, J. L.; Hemley, R. J.; Vaida, V. *J. Chem. Phys.* **1984**, *81*, 4218. (c) Vaida, V. *Acc. Chem. Res.* **1986**, *19*, 114.
- (27) McDiarmid, R.; Sheybani, A. H. *J. Chem. Phys.* **1988**, *89*, 1255.
- (28) Hoffmann, R.; Woodward, R. B. *Acc. Chem. Res.* **1968**, *1*, 17-22.
- (29) Woodward, R. B. *Aromaticity*; Special Publication No. 21; The Chemical Society: London 1967; pp 217-249.

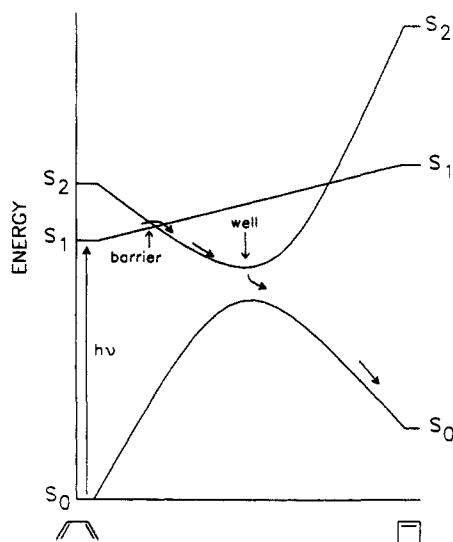


Figure 1. Simplified state correlation diagram for the concerted synchronous disrotatory ring closure of 1,3-butadiene.

barrier and well on the potential surface for symmetric disrotatory closure of 1,3-dienes controlled this photochemical reaction. These ideas have been extended to apply to a variety of photochemical reactions.³¹ A more extensive calculation qualitatively confirmed the results of Oosterhoff's seminal paper.³² A representation of the resulting calculations can be shown by using a state correlation diagram for electrocyclic disrotatory closure (Figure 1).

The calculations and correlation diagram suggest that for photochemical closure to occur a molecule must first pass over a 5–8-kcal/mol barrier before entering the neighboring 4–8-kcal/mol well that leads to ground-state product. It should be pointed out that this correlation diagram is predicated upon the ordering of the singlet excited states, but after several years of controversy the ordering indicated above seems to be established.³³ The excited-state barrier in this model would predict a temperature dependence for the photochemical closure of 1,3-dienes.

Calculations with CI but a small basis set have found a barrier for excited-state electrocyclic opening but not for the photochemical closure.³⁴ Of the two best calculations to date, one^{33c} gives about 11 kcal/mol for the energy difference between the first (1^1B_2) and the second (2^1A_1) vertically excited states of *s*-cis-1,3-butadiene while the other gives a much larger difference of >30 kcal/mol.^{33d} Both of these calculations show a much larger $1^1B - 2^1A$ splitting for the *s*-cis than for the *s*-trans conformer. If the first excited state increases in energy at roughly the same rate as the second excited state decreases during the course of the reaction, the former calculations would predict an excited-state barrier of roughly 4–5 kcal/mol, while the latter would suggest an even higher barrier. Very recent medium-level calculations on the excited-state surfaces for both 1,3-butadiene conformers found a very flat surface for the torsion of all C–C bonds in the 2^1A_1 .¹² However, these authors explain that they do not find the correct ordering of the excited states obtained by the "more extensive calculations" of Davidson^{33c} and Nakatsuji.^{33d} Because their incorrectly ordered excited states do not cross, they naturally find no excited-state barrier. Thus, the ordering of the excited states established both by calculations and electron-impact experiments³³ supports a barrier to synchronous electrocyclic closure.

We will suggest below, however, that the presence or absence of this barrier along this pathway may be a mute point since other pathways to electrocyclic closure are possible.

We report here low-temperature photochemical studies on *s*-cis acyclic 1,3-dienes that delineate the photochemistry of this species with regard to the two major photochemical reactions and enable us to make predictions concerning a potential energy surface combining these two events.

Experimental Section

Isoprene (Gold Label), (*E,E*)-2,4-hexadiene, (*E*)-1,3-pentadiene, and 2,3-dimethyl-1,3-butadiene were purchased from Aldrich and used without further purification. 2-Isopropyl-1,3-butadiene was prepared by $LiAlH_4$ reduction of isopropylethylacetoacetate obtained from Fluka Chemicals, followed by treatment with *p*-toluenesulfonyl chloride and elimination of the resulting ditosylate. Final purification was performed by using preparative gas chromatography. (*E,E*)-1,4-Dideuterio-2,3-dimethyl-1,3-butadiene (DDMB) was prepared by brominating the parent diene followed by elimination with potassium *tert*-butoxide of the tetrabromide to give a mixture of the dibromides. The (*E,E*)-dibromide (mp 36 °C) was separated and purified by crystallization from methanol. Its structure was confirmed by X-ray analysis. Deuteration of the dibromide followed the method of Stephenson,³⁵ but a Zn–Ag³⁶ rather than a Zn–Cu couple was used because the reaction proceeded at lower temperatures and led to less double bond isomerization. In a typical reaction silver acetate (0.16 g, 0.972 mmol) was added to 135 mL of glacial acetic acid under N_2 and warmed to 70 °C to dissolve the silver acetate. Zinc dust (4.75 g, 72.6 mmol) was added quickly to the warmed flask and the mixture was stirred for 5 min. The acetic acid was filtered off, and the zinc couple was washed eight times with 100 mL of H_2O . The last wash gave a negative halide test with 5% $AgNO_3$. Residual H_2O was eliminated from the couple by three washings with dry acetone followed by a D_2O rinse and then three washings with dry acetone and three washings with dry diethyl ether. The zinc couple was then dried under vacuum for 24 h. (*E,E*)-1,4-Dibromo-2,3-dimethyl-1,3-butadiene (3.04 g, 12.67 mmol) was dissolved in 50 mL of bis(ethoxyethyl) ether (distilled twice from Na) and then added to the zinc couple. All manipulations were performed under a dry N_2 atmosphere. The reaction was stirred at room temperature for 48 h. The reaction mixture was heated to 80 °C and the distillate collected at –78 °C. The distillate was washed twice with water, dried over Na_2SO_4 , and redistilled, collecting 0.94 mL (0.69 g, 8.12 mmol). Final purification was via preparative GC on a 32 ft 30% SE-30 3/8 in. column with an oven temperature of 50 °C giving a final yield of 38%. The NMR spectrum of the DDMB produced showed a 7:1 ratio of the (*E,E*) to (*E,Z*) isomers. DDMB produced at the elevated temperatures necessary when the Zn–Cu couple was used showed a 2:1 ratio of these isomers.

A Digilab FTS-15B FT-IR, Perkin-Elmer 552A UV/VIS spectrophotometer and a WM-250 or an AM-400 Bruker NMR spectrometer were used to obtain the spectral data. A 1000-W Xe(Hg) arc lamp was used as the light source for all experiments. Low-temperature IR spectra were taken by using an AirProducts CS-202 Displex equipped with an APD-E temperature controller. The Displex was fitted with external KBr windows and an internal CsI plate for the infrared experiments.

Samples were deposited diluted 1000:1 in argon or 40:1 in 3-methylpentane by passing the vapor through a quartz tube oven (3-mm i.d.) and letting the gas impinge upon the cooled CsI window. The oven temperature was measured with a chromel–alumel thermocouple placed in the flowing gas. Deposition rates for the samples codeposited with argon were maintained at 0.0026 mmol/h so that the contact time in the 4 cm long oven was 2.8 ms. NMR spectra of deposited samples were obtained by warming the system to room temperature overnight while pumping the argon/sample mixture through a liquid N_2 trap that was warmed and rinsed with NMR solvent to obtain the sample.

As previously shown for samples in argon,³⁸ photochemical efficiencies in 3-methylpentane of *s*-trans-*s*-cis isomerization and cyclobutene formation were obtained by deconvoluting, using a nonlinear least-squares calculation based on the general statistical method of Wentworth and Deming,³⁷ a series of UV spectra taken of a trapped mixture rich in the *cis* form after increasing photolysis times. The 40:1 3-methylpentane–DMB mixture was deposited to form a matrix with the same absorptivity

(30) Van der Lugt, W. Th. A. M.; Oosterhoff, L. J. *J. Am. Chem. Soc.* **1969**, *91*, 6042–6049.

(31) Michl, J. *Mol. Photochem.* **1972**, *4*, 243–255, 257–286, 287–314.

(32) Grimbirt, D.; Segal, G.; Devaquet, A. *J. Am. Chem. Soc.* **1975**, *97*, 6629–6632.

(33) (a) Hudson, B. S.; Kohler, B. E.; Schulten, K. In *Excited States*; Lim, E. C., Ed.; Academic Press: New York, 1982; Vol. VI, p 1. (b) McDiarmid, R. *J. Chem. Phys.* **1983**, *79*, 9. (c) Cave, R. C.; Davidson, E. R. *J. Phys. Chem.* **1987**, *91*, 4481. (d) Kitao, O.; Nakatsuji, H. *Chem. Phys. Lett.* **1988**, *143*, 528.

(34) Morihashi, K.; Kikuchi, O. *Theor. Chim. Acta* **1985**, *67*, 293.

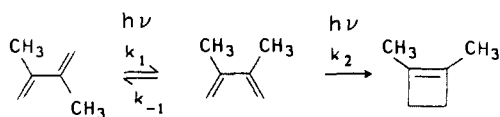
(35) Stephenson, L. M.; Gemmer, R. V.; Current, S. P. *J. Org. Chem.* **1977**, *42*, 212–214.

(36) Suggs, J. W. Thesis, Harvard University, 1976.

(37) (a) Wentworth, W. E. *J. Chem. Educ.* **1965**, *42*, 96. (b) Deming, W. E. *Statistical Adjustment of Data*; Wiley: New York, 1943.

(38) Squillacote, M. E.; Semple, T. C.; Mui, P. W. *J. Am. Chem. Soc.* **1985**, *107*, 6842.

Scheme 1



as the argon-DMB sample of our previously reported experiments.³⁸ The same light source mounted the same distance from the sample ensured that the light intensities would be essentially identical for the alkane and the argon matrix. We estimate that at most a 10% systematic difference in the light absorbed during the two experiments.

Results and Discussion

We have previously used a temperature jump conformational trapping technique³⁸⁻⁴⁰ that produces a mixture of the two diene conformations rich in the usually unobservable *s-cis* conformer. We felt that this observation presented a unique opportunity to investigate the photochemistry of the *s-cis* conformation. Thus matrix-isolated *s-trans-s-cis* mixtures of roughly 3:1 were produced from isoprene, 2-isopropyl-1,3-butadiene, *trans*-pentadiene, *trans,trans*-2,4-hexadiene, and 2,3-dimethyl-1,3-butadiene (DMB) by depositing from an oven temperature of 868 K onto the CsI window cooled to 19.3 K.⁴¹ Bands not present in room temperature depositions were observed in each case and assigned to the *s-cis* conformer.⁴²

Photolysis of Acyclic 1,3-Dienes. Upon photolysis of the argon matrices at 15 K all of the dienes were converted to their respective cyclobutenes, which were identified by previously reported IR spectra⁴³ or by comparing NMR spectra of the photolyzed sample with the NMR spectra of authentic cyclobutene. A photochemical *s-cis-s-trans* isomerization³⁸ allowed us to completely convert the conformational mixtures of isoprene, 2-isopropyl-1,3-butadiene, and DMB to their respective cyclobutenes.⁴⁴ Isoprene and 2-isopropyl-1,3-butadiene showed a very rapid *s-cis-s-trans* photoisomerization similar to that of the parent 1,3-butadiene.³⁹ This conformational photoisomerization was much more rapid than electrocyclic closure. Because the output of the Xe(Hg) lamp used falls off rapidly toward shorter wavelengths and because both of these dienes have a red-shifted *s-cis* form, a photostationary state was quickly established that was almost completely *s-trans*. However, 2,3-dimethyl-1,3-butadiene (DMB) showed a very slow *s-cis-s-trans* interconversion.³⁸ While the reasons for this dichotomy of behavior of these dienes are not clear, the slow conformational photoisomerization of DMB allowed us to examine the photochemistry of an *s-cis* isomer directly. We could therefore address the issue of the apparent contradiction between the observed electrocyclic closure at 15 K and the substantial barrier on the excited-state surface predicted by the simple state correlation diagram.

Because the photolyses were carried out at temperatures between 10 and 20 K, a vibrationally cold electronically excited molecule could not surmount even a 1-kcal/mol barrier. To examine the possibility of the involvement of vibrationally hot excited states, DMB was photolyzed in an alkane glass of 3-methylpentane at 15 K. The efficiencies of the photochemical

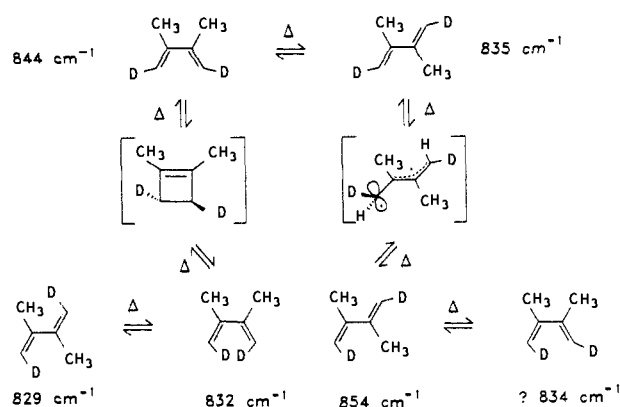


Figure 2. Schematic of the thermal isomerization pathways for (*E,E*)-DDMB. The wavenumbers shown with each isomer correspond to their CHD asymmetric wag.

events for DMB could be obtained as previously shown³⁸ by deconvoluting a series of UV spectra taken of a trapped mixture after increasing photolysis times. The efficiencies of the photochemical events of the following scheme were $k_1 = 2.1 \times 10^{-3} \text{ s}^{-1}$, $k_{-1} = 3.9 \times 10^{-4} \text{ s}^{-1}$, and $k_2 = 2.4 \times 10^{-2} \text{ s}^{-1}$, which are essentially identical with those obtained previously in argon³⁸ when the possible small difference in light absorption between these two experiments is taken into account (see Experimental Section for details). The importance of the "cooling" effects of an alkane matrix has been clearly demonstrated⁴⁵ so the lifetime of a vibrationally hot molecule in an excited state should be substantially shortened in an alkane matrix as compared to that in an argon matrix. In our case this alkane matrix "cooling" effect would have had a profound effect on the photochemical efficiencies of *s-cis-s-trans* isomerization versus closure. Because these efficiencies show no matrix dependence, predominant intervention of hot vibrational modes in photoproduct formation is ruled out. This result is perhaps not surprising given the relative floppiness and therefore good vibronic-matrix coupling possibilities present in DMB. Thus it appears that cyclobutene formation is a barrierless or near-barrierless process for excited-state dienes contrary to the simple state correlation diagram picture.

We could further take advantage of the slow *s-cis-s-trans* photochemical interconversion of DMB by investigating the photochemistry of (*E,E*)-1,4-dideuterio-2,3-dimethyl-1,3-butadiene (DDMB). This compound allowed us to examine photochemical double bond isomerization of both single bond isomers concurrently with cyclobutene formation. As a sidelight we were also able to examine the thermal double bond isomerization process.

CHD Wag Band Assignments for DDMB Isomers. When (*E,E*)-DDMB (1:1000 in argon) was deposited from room temperature the IR spectrum observed closely matched that of DMB³⁸ except for some isotope-shifted bands in the C-D stretching region (2340 cm^{-1}) and the most intense peak representing the asymmetric CHD wag of the isomer at 835 cm^{-1} (CH_2 wag of DMB at 893 cm^{-1}). From subsequent high-temperature depositions (vide infra) a smaller peak at 854 cm^{-1} could be assigned to the (*E,Z*)-DDMB CHD wag as would be expected since the major impurity reported by Stephenson using his Zn-Cu couple method is caused by isomerization of the double bond during deuterium incorporation. Indeed we used a Ag activated zinc because the higher temperatures necessary for reaction of the Zn-Cu couple led to greater isomerization. The ratio of the CHD wagging bands of the *s-trans* forms of the two double bond isomers was 6.7:1, very close to the 7:1 ratio of the two isomers as determined by ¹H and ²H NMR. We have shown previously that the absorptivities of the CH_2 wag of DMB is nearly the same for the *s-cis* and *s-trans* forms, and these further results seem to corroborate the insensitivity of the absorptivity of this band to geometry changes. However, higher temperature depositions show that the

(39) Squillacote, M. E.; Sheridan, R. S.; Chapman, O. L.; Anet, F. A. L. *J. Am. Chem. Soc.* **1979**, *101*, 3657-3659.

(40) Anet, F. A. L.; Squillacote, M. E. *J. Am. Chem. Soc.* **1975**, *97*, 3243-3244.

(41) Semple, T. C. Ph.D. Thesis, Brown University, 1987.

(42) In some cases (DMB and isoprene³⁸ and 2-isopropyl-1,3-butadiene) neat depositions from high temperatures were performed and the decay of the *s-cis* bands monitored. The *s-cis-s-trans* activation energy for 2-isopropyl-1,3-butadiene (4.3 kcal/mol) compared well with the two previously reported barriers for 1,3-butadiene³⁹ and isoprene³⁸ of 4.0 kcal/mol each and was larger than that of DMB, 3.4 kcal/mol, implying a substantially planar form for *s-cis*-2-isopropyl-1,3-butadiene. That the isopropyl group adopts a geometry which allows the diene moiety to be planar is confirmed by the large red shift (13 nm) in the UV of the *s-cis* conformer as compared to that of the *s-trans*.

(43) Srinivasan, R. *J. Am. Chem. Soc.* **1969**, *91*, 7557-7561.

(44) A future paper will deal with this unexpected *s-trans-s-cis* photochemical interconversion.

(45) LeBlanc, B. F.; Sheridan, R. S. *J. Am. Chem. Soc.* **1988**, *110*, 7250 and references cited therein.

wavelength of this band is very sensitive to geometry and isotope substitution and, as will be seen, the methylene wag band could be identified for nearly all single and double bond isomers of DDMB (see Figure 2 for these assignments).

Stephenson et al.^{35,46} showed that thermal isomerization of (*E,E*)-1,4-dideuterio-1,3-butadiene proceeded through two mechanisms. The first equilibrated the (*E,E*) and the (*Z,Z*) isomers via a conrotatory closure to cyclobutene followed by a conrotatory re-opening in the opposite sense. The second occurred at higher temperatures and equilibrated the (*E,E*) with the (*E,Z*) isomer via an allylmethylene biradical. We see similar thermal isomerizations for DDMB as pictured in Figure 2.

Deposition from 878 K showed two new bands in the CHD wag region, a strong band at 844 cm⁻¹ and a smaller one at 829 cm⁻¹. The ratios of the relative intensities of the bands in this region were 0.16, 0.44, 1.0, and 0.09 for the 854-, 844-, 835-, and 829-cm⁻¹ bands, respectively. Conformational trapping experiments on DMB³⁸ suggest that the band at 844 cm⁻¹ corresponds to the *s*-cis conformer of (*E,E*)-DDMB, an assignment confirmed by subsequent photolysis experiments. These same photolysis experiments show that the 829-cm⁻¹ band is due to an *s*-trans isomer, and Stephenson's experiments on the parent compound suggest that this band is due to the *s*-trans (*Z,Z*)-DDMB isomer since this is the product of the lowest energy double bond isomerization pathway. If these assignments are correct and if the intensities of the CHD wags of the three *s*-trans double bond isomers are indicative of the ratio of the isomers, then, noting that the ratio of the three *s*-cis isomers will be identical with the ratio of the *s*-trans isomers, the vinyl region of the ¹H NMR spectrum should show a ratio of 1:0.156 of the *Z* to *E* hydrogens. The integrated ¹H ratio was 1:0.151, confirming the assignment and showing that as expected the absorptivities of the CHD wags must be nearly identical for all isomers.

It should be noted that the ratio of the 854-cm⁻¹ band to the sum of the 835- and 829-cm⁻¹ bands was the same as the original (*E,Z*)- to (*E,E*)-DDMB ratio, showing that very little isomerization is occurring via the allylmethylene biradical at the 878 K deposition temperature. This is not true at higher deposition temperatures. A deposition of DDMB from 1060 K shows the same four bands in the CHD wag region with an additional band at 832 cm⁻¹. However, the intensities are substantially different, with relative band intensities of 0.74, 0.64, 1.0, 0.50, and 0.78 observed for the 854-, 844-, 835-, 832-, and 829-cm⁻¹ bands, respectively, showing a strong increase in the amount of (*E,Z*) isomer. These results imply that there is now a substantial amount of isomerization occurring via both mechanisms. If the ratio of intensities of the bands of the three *s*-trans isomers at 854, 835, and 829 cm⁻¹ are indicative of the relative amounts of the three isomers, the ¹H NMR spectrum should show a 1:0.841 ratio of the *Z* to *E* hydrogens. When the sample is warmed and trapped, the NMR spectrum shows a 1:0.844 integrated ratio, which corroborates the IR assignment and implies that the new band at 832 cm⁻¹ represents a CHD wag of an *s*-cis form and is in fact the *s*-cis-(*E,Z*)-DDMB (vide infra).

Final confirmation of the IR assignments comes from a photolysis experiment on a sample deposited from 878 K. This matrix-isolated sample, which contains mostly the *s*-cis and *s*-trans conformers of (*E,E*)-DDMB and small amounts of both the (*E,Z*) isomer as initial impurity and of the (*Z,Z*) isomer produced from the electrocyclic closing and re-opening mechanism, showed interesting photochemistry. Initially the bands at 844 and 835 cm⁻¹ decayed with an increase of the bands at 854 and 832 cm⁻¹. Further photolysis showed the band at 829 cm⁻¹ growing at the expense of intensity of the other bands and some broadening of the band at 835 cm⁻¹. Continued photolysis caused the disappearance of the bands at 844 and 832 cm⁻¹ with bands at 1110 and 1289 cm⁻¹, which belong to 1,2-dimethylcyclobutene-*d*₂ now appearing. When the irradiation was continued the remaining bands at 854, 835, and 829 cm⁻¹ slowly disappeared with a concomitant increase in the dimethylcyclobutene bands.

The explanation of these photochemical events is based on our previous photochemical results for DMB³⁸ where we saw closure of the *s*-cis form to 1,2-dimethylcyclobutene followed by a slower conversion of the *s*-trans form. In this case, these events are preceded by photochemical isomerization of double bonds. Initially the predominant *s*-trans (*E,E*) isomer (835 cm⁻¹) is converted to the *s*-trans (*E,Z*) isomer (854 cm⁻¹) and the *s*-cis (*E,E*) (844 cm⁻¹) to the (*E,Z*) *s*-cis, which confirms the 832-cm⁻¹ band as the *s*-cis-(*E,Z*)-DDMB. With continuing photolysis, the *s*-trans (*E,Z*) conformer is converted to the *s*-trans conformer of the (*Z,Z*) isomer thereby increasing the intensity of the 829-cm⁻¹ band. Presumably the *s*-cis (*Z,Z*) is also produced, but we see no distinct band though broadening of the 835-cm⁻¹ band suggests the (*Z,Z*) *s*-cis may be masked by this peak. The assignment of the *s*-cis form bands at 844 and 832 cm⁻¹ is nicely confirmed by continued irradiation, which converts the *s*-cis isomers to 1,2-dimethylcyclobutene leaving only the *s*-trans bands which disappear at a much slower rate.

Thermal Isomerization of DDMB. The CHD wag assignments allow us to examine the thermal diene double bond isomerization by monitoring the band intensity as the deposition temperature changes. The electrocyclic conrotatory closing and re-opening pathway could be examined by following the intensities of the *s*-trans-(*E,E*)-DDMB band at 835 cm⁻¹ and the (*Z,Z*) band at 829 cm⁻¹. With a deposition temperature of 878 K the intensity of the 829-cm⁻¹ band of *s*-trans-(*Z,Z*)-DDMB showed that the equilibration between the (*E,E*) and the (*Z,Z*) isomers was about 16% complete. An oven residence time can be calculated from the deposition rate and the pressure in the oven to be 2.8 ms so that an equilibration rate can be calculated from the amount of equilibration that has occurred during passage through the oven. Thus a barrier for the thermally allowed closure of DDMB to the cyclobutene is calculated to be 47 kcal/mol. From the IR spectra of a sample deposited at 933 K a barrier of 49 kcal/mol was measured. At higher temperatures essentially complete equilibration had occurred. The average barrier of 48 kcal/mol can be compared to the reported barrier for butadiene of 44.5 kcal/mol.^{35,46}

Single double bond thermal isomerization through the allylmethylene biradical does not occur at 878 K since no additional (*E,Z*) isomer is produced and only very small amounts at 933 K, but at 1060 K 60% equilibration of rotation about a single bond had occurred, which corresponds to a barrier of 55 kcal/mol. Similar results for a deposition from 1100 K led to a barrier of 56 kcal/mol. Thus the barrier for allylmethylene biradical formation in DDMB is about 55 kcal/mol, as compared to the reported barrier for 1,3-butadiene of 52.2 kcal/mol.^{35,46}

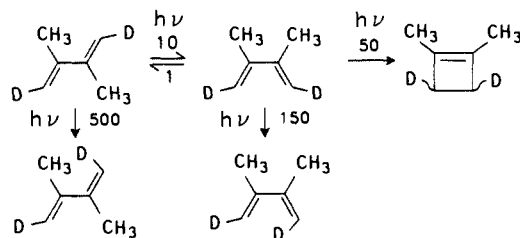
Photochemistry of DDMB. The results of the photolysis of DDMB deposited from 898 K imply that both double bond rotation and electrocyclic closure occur from the *s*-cis conformer, as both photoequilibration of *s*-cis isomers and cyclobutene production is seen. It should also be pointed out that the initial *s*-trans (*E,E*) isomer is converted to the (*E,Z*) *s*-trans isomer as is apparent by photolysis of a sample deposited from room temperature where decay of the 835-cm⁻¹ band is accompanied by an increase in the 854-cm⁻¹ band. Similarly photolysis of samples deposited from higher temperatures shows that the *s*-cis (*E,E*) isomer is involved in a double bond isomerization process with the *s*-cis (*E,Z*) isomer. Thus, the proposed H.T.-n type mechanism¹⁵ is not operative in this case, but unlike the rhodopsin system there is essentially no volume change during the photoisomerization of the double bonds of DDMB (a H is exchanged for a D) so the "space saving" driving force for the H.T.-n mechanism is absent.

It is not possible to obtain from just the infrared data the relative efficiencies from the *s*-cis isomer for the two photochemical events because overlap with *s*-trans bands prevents accurate measurement of the intensities of the CHD wags of the *s*-cis (*E,Z*) and (*Z,Z*) isomers. To surmount this problem NMR spectra of photolyzed matrix-isolated samples were obtained.

A DDMB/argon mixture (1:1000) was deposited from 878 K onto a CsI plate at 19.4 K. Photolysis of this sample led as before to cyclobutene formation as well as photoequilibration of all *s*-trans

(46) Stephenson, L. M.; Brauman, J. I. *Acc. Chem. Res.* 1974, 7, 65.

Scheme II



isomers and of all *s*-cis isomers. The IR spectrum before photolysis showed a ratio of intensities of the 854-, 835-, and 829-cm⁻¹ bands to be 1.0, 0.18, and 0.11, which assuming nearly identical absorptivities of these *s*-trans bands would give a NMR ratio of the *E*:*Z* hydrogens of 1.0:0.164. The NMR spectra of a sample prepared identically but not photolyzed showed a ratio of 1.0:0.163.

After 2.5 h of photolysis the IR spectra of the sample showed a 1:1:0.65 ratio of intensities of the *s*-trans isomers. A decrease in the *s*-cis (*E,E*) 844-cm⁻¹ band was accompanied by a concurrent rise in the area representing the other *s*-cis isomers between the 835- and 829-cm⁻¹ *s*-trans peaks. A rise in the IR bands identified as those of the cyclobutene photoproduct occurred simultaneously. With the prephotolyzed conformational mixture being enriched by 32% in the (*E,E*) *s*-cis form, the drop in intensity of the 844-cm⁻¹ band upon photolysis represents 6.2% of the total amount of DDMB present in the matrix. After photolysis the matrix-isolated sample was warmed and the DDMB and cyclobutene present were trapped. Subsequent high-field NMR spectra showed 1.6% cyclobutene photoproduct, thus the other 4.6% of the *s*-cis (*E,E*) isomer must have either undergone double bond isomerization and become *s*-cis (*E,Z*) or undergone single bond rotation to *s*-trans (*E,E*). However, our previous results with DMB³⁸ in an argon matrix and our current results in a 3-methylpentane matrix show that *s*-cis DMB closes to cyclobutene about 50 times more efficiently than it photoisomerizes to the *s*-trans isomer. Assuming this ratio does not change drastically in the deuterated analogue, then nearly all the *s*-cis (*E,E*) isomer not converted to cyclobutene is photoisomerized to the *s*-cis (*E,Z*) isomer. In turn this isomer may undergo further photoisomerization to the *s*-cis (*Z,Z*) isomer. The ratio for cyclobutene production to double bond isomerization is, then, 1:2.9. This experiment was repeated two more times and in both instances gave a ratio within 10% of the initial value. While we cannot strictly quantify this ratio with IR spectroscopy, it is consistent with the intensities of the cyclobutene bands and the increase in the (*E,Z*) and (*Z,Z*) *s*-cis isomers shown by the increase of the 832-cm⁻¹ band and the additional broadening underneath the *s*-trans band at 835 cm⁻¹. Thus we can show for the first time that an *s*-cis isomer of an acyclic diene undergoes both major photochemical events, electrocyclic closure and double bond isomerization. It may be that this dichotomy was actually evident earlier. When *trans*-penta-1,3-diene is photolyzed with 254-nm light a 1:2.8 ratio of closure to isomerization is seen, but with irradiation at 229 nm no closure is apparent.⁷ While these results were initially interpreted to wavelength-dependent photochemistry,⁷ we have shown that the *s*-cis conformer of *trans*-penta-1,3-diene is the primary absorbing species at 254 nm.⁴¹ Therefore, these results corroborate our ratio of 1:2.9 for *s*-cis-DDMB. When the results for the efficiencies of *s*-cis-*s*-trans photoisomerization and electrocyclic closure obtained from deconvolution of photolyzed DMB UV spectra³⁸ are combined with the measured rates of double bond isomerization of the *s*-trans form, the relative efficiencies of the various photochemical events can be delineated as seen in Scheme II.

It is interesting that our results show that double bond isomerization and cyclobutene production are competitive processes even at 20 K. Isomerization, which presumably partitions equally between starting material and product, occurs only about six times more often than electrocyclic closure. Further, our results in the 3-methylpentane matrix suggest that these events derive from vibrationally cool excited states. While it has not been definitely established, most calculations seem to suggest little or no barrier

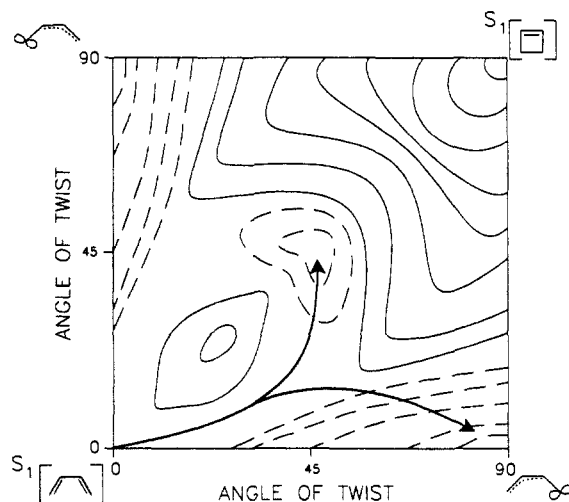


Figure 3. Proposed potential energy surface for the S_1 state of an *s*-cis diene based on energy diagrams of ref 25, 32, and 33c showing a pathway for double bond isomerization and a nonsynchronous pathway for ring closure. Solid and dashed contours represent energies above and below that of the vertically excited state, respectively.

to photochemical double bond isomerization.^{12,25} At the same time calculations for disrotatory electrocyclic closure show a substantial barrier.^{32,33c,d} How can one explain a vibrationally cold molecule on the excited-state surface surmounting, at 20 K, a supposed 4–8-kcal/mol barrier to closure as a competitive process to a barrierless rotation? Calculations with a small basis set but substantial CI suggested that no barrier existed for the photochemical synchronous closure in either a disrotatory or conrotatory manner.³⁴ However, the mechanism proposed by these authors demanded an equilibrium between conrotatory and disrotatory wells on the excited-state surface, an unlikely situation at our temperatures.

There is, however, quite literally another way around this barrier. A possible excited-state surface (pictured in Figure 3) shows that a nonsynchronous closure, which avoids the barrier of the synchronous disrotatory reaction, could occur.

In the surface presented, each axis represents a 90° barrierless rotation around a terminal double bond leading to an allylmethylene species. The diagonal corresponds to the concerted disrotatory synchronous reaction forming cyclobutene. This path has a barrier, and a well leading to the ground-state cyclobutene surface. This quadrant of the entire surface and its mirror image would describe a disrotatory mode of closure while the other two quadrants of this simplified surface would represent an excited-state conrotatory closure. The central well of these latter two quadrants would presumably be lacking⁵⁰ or be only very shallow.³⁴

The reaction path presented avoids the barrier of 4–8 kcal/mol by initially rotating around only one of the double bonds. Continuation of this rotation leads to a well that represents an allylmethylene zwitterionic species and thus eventual double bond isomerization. If on the other hand the other double bond now starts to rotate, the path leads into the central well which communicates with the cyclobutene ground state. This pathway represents a concerted nonsynchronous^{47,48} photochemical closure to a cyclobutene and bypasses the barrier present on the synchronous pathway. This surface also has the added attractiveness of combining electrocyclic closure and double bond isomerization onto one potential surface, as indeed they must be, since they derive

(47) Dewar, M. J. S.; Pierini, A. B. *J. Am. Chem. Soc.* **1984**, *106*, 203–208.

(48) Dewar, M. J. S. *J. Am. Chem. Soc.* **1984**, *106*, 209–219.

(49) (a) Bonacic-Koutecky, V.; Koutecky, J.; Michl, J. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 170. (b) Dolbier, W. R.; Matsui, K.; Dewey, H. J.; Horak, D. V.; Michl, J. *J. Am. Chem. Soc.* **1979**, *101*, 2136.

(50) A three-dimensional potential surface has been discussed for the *s*-trans isomer: Baratz, B. H.; Singh, A. K.; Liu, R. S. H. *Nouv. J. Chim.* **1981**, *5*, 297–303.

from the same excited state of the *s*-cis conformer.

Although nonsynchronous pathways of this type, which might be expected to occur around this conical intersection of surfaces, have been suggested for cyclobutene formation,^{30,49} these studies have not taken the next step of combining the closure with double bond isomerization.⁵⁰ According to a potential surface of the type suggested, the relative yields of double bond isomerization and cyclobutene formation would be determined by the dynamics of the surface at the point where the two pathways diverge rather than by the presence of a barrier. Note also that the barrierless nonsynchronous closure pathway may be preferred even if there is no barrier to the synchronous closure, because again presumably the surface dynamics will determine the route along the surface that an excited molecule would take. Most importantly, this combined surface also suggests that the cyclobutene formation-double bond isomerization partitioning of an *s*-cis acyclic 1,3-diene would be strongly influenced by the stability of the zwitterionic excited state produced from the *s*-cis conformer. Further work on low-temperature photochemistry of 1,3-dienes is being carried out to investigate this supposition.

Summary

We have shown that the thermal chemistry of double bond rotation of 2,3-dimethyl-1,3-butadiene is similar to that of 1,3-butadiene in that two mechanisms exist: a cyclobutene closure and reopening mechanism with a barrier of 48 kcal/mol and a pathway via an allylmethylene biradical with a barrier of 55 kcal/mol. Both of these barriers are slightly higher than those of the parent compound, 1,3-butadiene.³⁵

We have shown that several acyclic 1,3-dienes photochemically close at low temperatures despite a predicted barrier to the synchronous disrotatory closure on the excited-state surface. A dideuterio derivative of 2,3-dimethyl-1,3-butadiene was used to show that the *s*-cis conformer undergoes both major photochemical events, double bond isomerization and electrocyclic closure in roughly a 3:1 ratio. An excited-state potential surface was described that combines these two processes and allows a non-synchronous disrotatory closure pathway. This surface suggests that the electrocyclic closure-double bond isomerization ratio from the *s*-cis conformer of an acyclic diene may depend greatly upon the energy of the allylmethylene excited state.

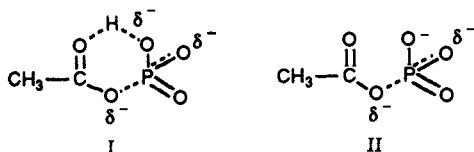
Divalent Metal Ion Catalyzed Reactions of Acyl Phosphates

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Abstract: The hydrolysis of the acyl phosphate, 1,10-phenanthroline-2-carbonyl phosphate, proceeds with a hydroxide ion catalyzed reaction of the dianionic species at high pH, a pH-independent reaction of that species in the pH range 7-10, and a reaction of the zwitterionic species (protonated phenanthroline nitrogen) at pH < 6 ($pK_{app} = 5.6$). The divalent metal ions Cu^{2+} , Ni^{2+} , Co^{2+} , and Zn^{2+} have a large effect on the rate of hydrolysis. At saturating concentrations of Ni^{2+} , Co^{2+} , and Zn^{2+} (0.003 M, 50-fold excess over the acyl phosphate), hydroxide ion catalyzed reactions occur that are $>10^7$ -fold more favorable at 30 °C than in the absence of the metal ions. Likewise, Mg^{2+} exerts a sizable catalytic effect ($>10^4$), although binding is considerably weaker than with the other metal ions (saturation only occurs at Mg^{2+} concentrations greater than 0.1 M). The cupric ion promoted OH^- -catalyzed reaction at 30 °C (0.002 M Cu^{2+}) is (5×10^{10})-fold more favorable than OH^- catalysis in the absence of the metal ion. At pH < 4 a Cu(II)-promoted pH-independent reaction takes place that has a ΔS^\ddagger of -34.3 eu. Incorporation of ^{18}O into the carboxylic acid product when the hydrolytic reactions were carried out in ^{18}O -enriched water showed conclusively that C-O bond breaking occurs in the metal ion promoted hydroxide ion and pH-independent processes. Both imidazole and pyridine are catalysts in the hydrolysis of the acyl phosphate, and the imidazole-catalyzed reaction is markedly enhanced by a saturating concentration of Ni^{2+} . The effect of the metal ion is much smaller in the reaction with pyridine; the second-order rate constant for the pyridine reaction is only increased 3-fold by the presence of a saturating concentration of Ni^{2+} . Thus, the strongly chelated metal ions greatly facilitate nucleophilic reactions that occur at the carbonyl carbon of the acyl phosphate rather than metaphosphate elimination or nucleophilic attack at phosphorus.

Acyl phosphates are phosphoric acid derivatives of considerable biological importance.² The hydrolysis reactions of acetyl phosphate have been extensively investigated.³⁻⁶ Evidence was presented by Di Sabato and Jencks⁶ in support of an elimination mechanism in both monoanion (I) and dianion (II) hydrolysis in



which P-O bond breaking gives a hypothetical metaphosphate intermediate. Such an intermediate had been previously suggested

in the hydrolysis of alkyl and aryl phosphomonoesters,^{3,7,8} but there is no evidence that free metaphosphate is formed in aqueous solution.⁹⁻¹¹ At high pH, an OH^- -catalyzed reaction occurs with C-O bond breaking in the hydrolysis of acetyl phosphate.^{4,5}

Metal ions (Mg^{2+} , Ca^{2+} , and Li^+)^{3,4,12} were found to have only a small effect in the reactions of acetyl phosphate, as might be expected in the absence of an additional liganding group. The small effects at high metal ion concentrations have precluded

(7) (a) Bunton, C. A.; Llewellyn, D. R.; Oldham, K. G.; Vernon, C. A. *J. Am. Chem. Soc.* **1958**, 3574. (b) Butcher, W. W.; Westheimer, F. H. *J. Am. Chem. Soc.* **1955**, 77, 2420. (c) Kumamoto, J.; Westheimer, F. H. *J. Am. Chem. Soc.* **1955**, 77, 2515.

(8) Kirby, A. J.; Varvoglis, A. G. *J. Am. Chem. Soc.* **1967**, 89, 415.

(9) Bourne, N.; Williams, A. *J. Am. Chem. Soc.* **1984**, 106, 7591.

(10) (a) Skoog, M. T.; Jencks, W. P. *J. Am. Chem. Soc.* **1984**, 106, 7597.

(b) Herschlag, D.; Jencks, W. P. *J. Am. Chem. Soc.* **1986**, 108, 7938.

(11) Ramirez, F.; Marecek, J.; Minore, J.; Srivastava, S.; le Noble, W. J. *J. Am. Chem. Soc.* **1986**, 108, 348.

(12) (a) Oestreich, C. H.; Jones, M. M. *Biochemistry* **1966**, 5, 2926. (b) Klinman, J. P.; Samuel, D. *Biochemistry* **1971**, 10, 2126. (c) Briggs, P. J.; Satchell, D. P. N.; White, G. F. *J. Chem. Soc. (B)* **1970**, 1008. (d) See also Melhado, L. L.; Gutsche, C. D. *J. Am. Chem. Soc.* **1978**, 100, 1850. Lau, H.; Gutsche, C. D. *J. Am. Chem. Soc.* **1978**, 100, 1857.

(1) Postdoctoral fellow, University of Southern California.

(2) Stryer, L. *Biochemistry*, 2nd ed.; W. H. Freeman and Co.: San Francisco, 1981.

(3) Bruice, T. C.; Benkovic, S. *Bioorganic Mechanisms*, W. A. Benjamin: New York, 1966; Vol. 2 and references therein.

(4) Koshland, D. E., Jr. *J. Am. Chem. Soc.* **1952**, 74, 2286.

(5) Park, J. H.; Koshland, D. E., Jr. *J. Biol. Chem.* **1958**, 233, 986.

(6) Di Sabato, G.; Jencks, W. P. *J. Am. Chem. Soc.* **1961**, 83, 4393, 4400.