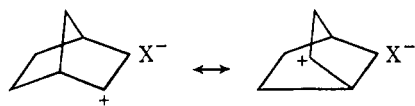


mides indicates that there is a fundamental electronic difference in the transition states that are involved. In view of the fact that this difference is in the direction that one would expect if participation during the ionization step occurred, we are forced to conclude that our findings provide compelling support for Winstein's⁴ suggestion that the transition states for the solvolysis of simple *exo*-norbornyl compounds are nonclassical.⁸

This conclusion is based on the following argument. For a classical norbornyl cation that arises from the solvolysis of an *exo*-oriented exophile, the secondary isotope effect (k_H/k_D) is approximately 1.18 ± 0.02 for two deuterium atoms. If the charge at C₂ is delocalized between C₁ and C₂ in the transition state, the magnitude of the effect would be diminished by a factor of $(1.18)^n$, where n is the fraction of the charge associated with C₂. For a transition state in which the resonance forms



are equal contributors, only one-half of the electronic charge would reside on C₂. The isotope effect that would be associated with a transition state approximating this situation would therefore be $(1.18)^{1/2}$ or 1.085; this value corresponds exactly to what was observed for the solvolysis of *exo*-norbornyl bromide.^{1,10}

(8) Brown⁹ has argued that, because parallels exist between the solvolysis rates of compounds that lead to classical norbornyl cations, the stereochemical fate of these cations, and the behavior of the parent norbornyl systems, these data cannot logically be used as a foundation for postulating nonclassical behavior for the parent system. Unfortunately, the perturbations that result from the conversion of a secondary system to a tertiary system introduces additional factors (e.g., new steric effects) that cloud the interpretation of data and cast doubt upon the validity of arguments based upon the analogous behavior of secondary and tertiary systems. The difference in secondary isotope effects for these two systems clearly demonstrates that tertiary norbornyl systems should not be used as models for the norbornyl cation.

(9) A summary of H. C. Brown's arguments along with numerous references to his papers can be found in *Chem. Eng. News*, **45**, 86 (Feb 13, 1967).

(10) It would be erroneous to conclude that the excellent agreement between the observed isotope effect and that calculated on the basis of the above model requires that in the transition state for solvolysis of simple *exo*-norbornyl derivatives the norbornyl fragment must be completely symmetrical. A transition state in which bridging was only one-third complete could not be distinguished from the above model due to the experimental uncertainties that are involved in the isotope effects.

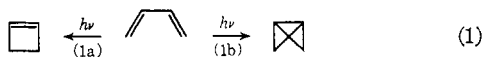
John P. Schaefer, James P. Foster
Michael J. Dagani, Linda M. Honig
Department of Chemistry, University of Arizona
Tucson, Arizona 85721

Received April 26, 1968

Mechanism of the Photochemical Valence Tautomerization of 1,3-Butadienes

Sir:

Irradiation of 1,3-butadiene is known to give rise to cyclobutene (1a) and bicyclo[1.1.0]butane (1b), the former being the major product.¹ While the experi-

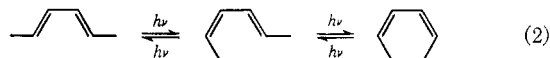


mental evidence strongly suggests that both processes

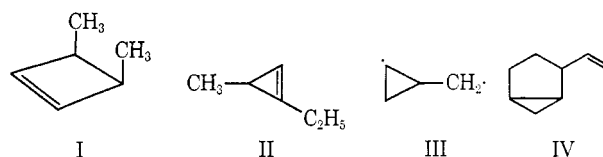
(1) R. Srinivasan, *J. Am. Chem. Soc.*, **85**, 4045 (1963).

occur from the excited singlet state of 1,3-butadiene,^{2a} the difference between the two reaction pathways has never been satisfactorily explained. On the basis of a study of the photoisomerization of the stereoisomers of 2,4-hexadiene, we propose that (1a) is a concerted process, while (1b) is most probably a stepwise reaction.^{2b}

The photoisomerizations of *trans,trans*-, *cis,trans*-, and *cis,cis*-2,4-hexadienes were studied in ether solution at 2537 Å. The stereoisomerizations indicated by (2) rapidly led to a photostationary state in which the concentrations corresponded to *trans,trans* 35.7%;



cis,trans 30.5%; *cis,cis* 33.7%. At the same time, four other isomers (mol wt by mass spectrometry = 82) were also formed more slowly. The most important of these amounted to 33% of the hexadiene that disappeared. Its ir (strong absorptions at 727, 2950, and 3020 cm⁻¹) and nmr spectra (τ 3.98 (2 H), singlet; ~ 7.1 (2 H), multiplet; 9.02 (6 H), doublet ($J = 7$ cps) with fine structure) when considered together with the fact that it isomerized cleanly at 180° to give *cis*-, *trans*-2,4-hexadiene showed that it was *cis*-3,4-dimethyl-



cyclobutene (I). The stereochemistry of the thermal decomposition of this molecule has already been demonstrated by Winter³ to be conrotatory.

The second isomer which accounted for about 5% of the hexadiene that disappeared had infrared absorptions at 1775 and 1725 cm⁻¹ (m) as well as at 1375 and 1360 cm⁻¹ (m). The nmr spectrum consisted of a broad (half-width 4 cps) absorption (1 H) at τ 3.45, an octet at 7.5 (2 H), and a complex absorption from 8.5 to 9.1 (7 H). In the 100-Mc spectrum,⁴ the last absorption could be resolved into an octet (1 H) at τ 8.6, a symmetric triplet at 8.86 (3 H), and a doublet at 8.99 (3 H). Decoupling experiments showed that the absorptions at τ 7.5 and 8.86 could be attributed to the CH₂ and CH₃ of an ethyl group while the proton at τ 8.6 and the three protons at 8.99 could be due to a >CHCH₃ group. The lone proton at τ 3.45 was coupled to all of these protons with coupling constants which ranged from 1.8 cps for the CH proton to 1.0 cps for the CH₃ of the ethyl group. The presence of an ethyl and a methyl group left only three carbons to account for. Two of these presumably formed the ends of an olefinic group while the third carbon was not olefinic. The infrared absorption at 1775 cm⁻¹ is quite close to the C=C stretching frequency in 1,3-dimethylcyclopropene⁵ of 1773 cm⁻¹. The structure which would fit all of these data is that of 1-ethyl-3-methylcyclopropene (II).

(2) (a) R. Srinivasan, *Advan. Photochem.*, **4**, 113 (1966). (b) It is assumed that the same mechanism is operative in the valence tautomerization of all linear 1,3-dienes.

(3) R. E. K. Winter, *Tetrahedron Letters*, 1207 (1965). We thank Dr. Winter for supplying us with the spectral data for I for comparison.

(4) We thank Dr. C. S. Yannoni of this laboratory for these spectra.

(5) G. L. Closs, *Advan. Alicyclic Chem.*, **1**, 74 (1966).

