

THE NATURE OF THE VINYLMETHYLENECYCLOPROPANE TO METHYLENECYCLOPENTENE REARRANGEMENT

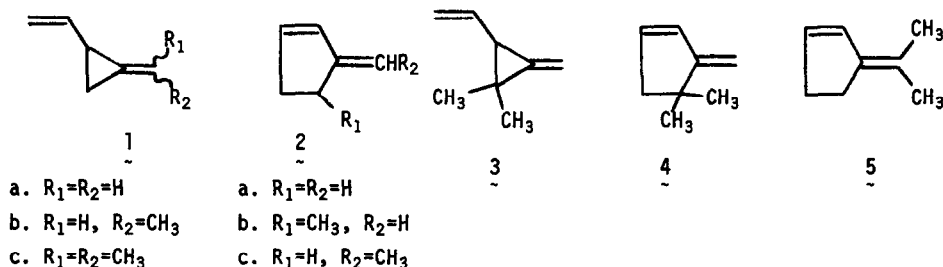
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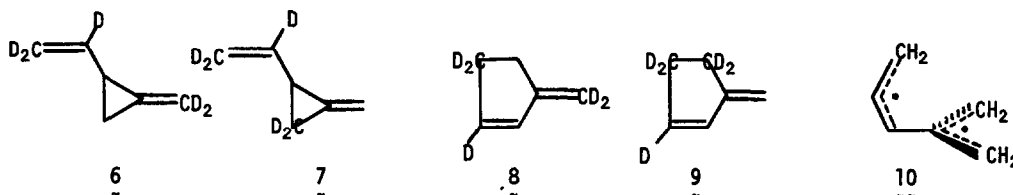
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Vinylmethylene cyclopropane (1a) undergoes thermal isomerization to 3-methylene cyclopentene (2a) at 80°, and the remarkable facile nature of the reaction prompted description of its mechanism as being a concerted [3,3]-sigmatropic process.¹ Subsequent reports that thermolysis of 1b furnishes a mixture of 2b and 2c² and that 1c affords 4 and 5³ suggest that the energy surface relating vinylmethylene cyclopropanes and methylenecyclopentenes may include concerted [1,3]- as well as [3,3]-sigmatropic pathways or their structural equivalents in the form of diradical processes. Kende, *et al.*, have proposed that the reaction proceeds *via* an orthogonal biradical,³ but owing to their use of methyl groups as skeletal labels, evaluation of the actual geometry of a diradical intermediate or of the possible competition between concerted sigmatropic processes is exceedingly difficult. Our own interest in the thermal energy surface of methylenecyclopropanes⁴ has prompted synthesis of the isotopically labeled derivative 6 in an effort to probe more completely the mechanism by which 2 is formed.⁵



Thermolysis of 6, the course of which was monitored by nmr analysis, revealed that the previously reported isomerization to 3-methylene cyclopentene (2a)¹ is accompanied by a competing degenerate methylenecyclopropane rearrangement that equilibrates 6 with 7 (an analogous isomerization interconverts 1c and 3).^{7,8} The latter reaction is about ten times faster than the former process [$\log k_d = 11.8 - (24900/2.303RT)$ vs $\log k_p = 11.4 - (25800/2.303RT)$]¹⁰ and

complicates our intended analysis considerably owing to the loss of the positional integrity in 6. Nevertheless, determination of the distribution of deuterium between carbon atoms 5 and 6 in the d_5 -3-methylenecyclopentenes 8 and 9 isolated from the thermolysis still provides valuable mechanistic information.



The first analysis was of a mixture of 8 and 9 that had been formed during a period of time when the equilibration of 6 and 7 had proceeded through about three half-lives; thus the *average* composition of the mixture of 6 and 7 that afforded the sample of 8 and 9 was about 70:30. The analysis revealed a *nearly equal* quantity of deuterium at carbon atoms 5 and 6, *i.e.*, the ratio of 8:9 was $1.020 \pm 0.014:1.0$, a value derived from the average of 16 integrations of the nmr spectrum. As 8 and 9 do not interconvert under the conditions of the experiment, the observed distribution requires that isomers 8 and 9 be formed in substantially the same amounts in a kinetically controlled process. Furthermore, because the equilibration of 6 and 7 was incomplete at the point of this first analysis, the distribution of label that is observed definitively *excludes* either the [3,3]- or the [1,3]-sigmatropic process as the *sole* mode for rearrangement. An alternative hypothesis that competing concerted [1,3]- and [3,3]-sigmatropic processes may be operating exclusively in the formation of 8 and 9 would require that the rates for the two modes be essentially identical, a coincidence that seems improbable because of the significantly different steric factors that appear to be involved in the two pathways. We believe that intervention of an orthogonal diradical identical to 10, except for the presence of deuterons, best rationalizes the distribution of deuterium found in the d_5 -3-methylenecyclopentenes 8 and 9.

Is, then, a geometrically symmetrical diradical the sole intermediate in the vinylmethylenecyclopropane rearrangement? Our results, although not as definitive as we would prefer, suggest not. Thus examination of a sample of 8 and 9 received from thermolysis of an *equilibrated* mixture of 6 and 7 provides a ratio of 8 to 9 of $0.976 \pm 0.032:1.0$ (average of fifteen integrations), a value that is slightly different from that obtained above. An analysis

of our experimental data by the t technique¹¹ allows rejection of the hypothesis that the deuterium distribution is identical in the mixture of 8 and 9 from the two pyrolyses at a confidence level greater than 99%; *i.e.*, a greater proportion of 8 is formed in the thermolysis of the equilibrated mixture than in the rearrangement of pure 5. The observation of time-dependent ratios of 8 and 9 may represent a minor concerted component to the rearrangement or may be the consequence of generation of diradicals that do not actually achieve the geometrical symmetry of 10. Differentiation between these possibilities is not possible on the basis of the data currently available.¹²

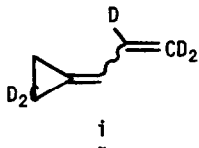
References and Footnotes

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1. T. C. Shields, W. E. Billups and A. R. Lepley, *J. Amer. Chem. Soc.*, 90, 4749 (1968).
- 2a. T. C. Shields, W. E. Billups, *Chem. Ind.*, 619 (1969).
- b. K. H. Leavell, W. E. Billups and E. S. Lewis, Abstracts, XXIIIth IUPAC Congress, Boston, Mass., July 26, 1971, Paper No. 108.
3. A. S. Kende and E. E. Riecke, *J. Amer. Chem. Soc.*, 94, 1397 (1972).
4. J. C. Gilbert and J. R. Butler, *ibid.*, 92, 2168 (1970).
5. A previous attempt to synthesize a specifically labeled derivative of 1 failed owing to the severity of the reaction conditions required for the Hofmann or Cope eliminations used to introduce the exocyclic double bond.⁶ Our synthesis began with the addition of diazopropyne to methyl α -bromoacrylate and was completed by a reductive debromosylation analogous to that previously reported.⁴
6. H. D. Roth, Abstracts, 159th Meeting, American Chemical Society, Houston, Texas, February 1971, No. PET. 002.
7. Hydrocarbon 5 was heated at 60-90° as a degassed 40% solution in carbon tetrachloride contained in an nmr tube. The kinetics were evaluated by multiple integrations of the nmr spectrum as was the distribution of deuterium in the products.
8. Neither of the reactions involves intermediacy of allylidene cyclopropane (1), as no nmr

References and Footnotes (cont.)

resonances corresponding to it can be detected; if 1 were being generated, it would accumulate during the thermolysis since the E_a for rearrangement of this type of system is anticipated to be greater than 32 kcal/mol.³ Thus, the vinyl group may be added to the list⁹ of substituents that impart high or total positional selectivity to the methyl-encyclopropane rearrangement.



9. W. von E. Doering and H. Roth, *Tetrahedron*, 26, 2825 (1970).
10. The $\Delta\Delta H^\ddagger$ of 0.9 kcal/mol that separates the transition states for the degenerate and the irreversible rearrangements may simply be a reflection of the anticipated difference in the ground state energies of the *syn* and the *anti* conformers of 6. The former, less stable conformer is the one that possesses the geometry appropriate for ultimate transformation to 8 and 9.
11. Q. McNemar, "Psychological Statistics," 4th Ed., John Wiley and Sons, Inc., 1969, Chapter 7.
12. The support of this research by the Robert A. Welch Foundation is gratefully acknowledged.