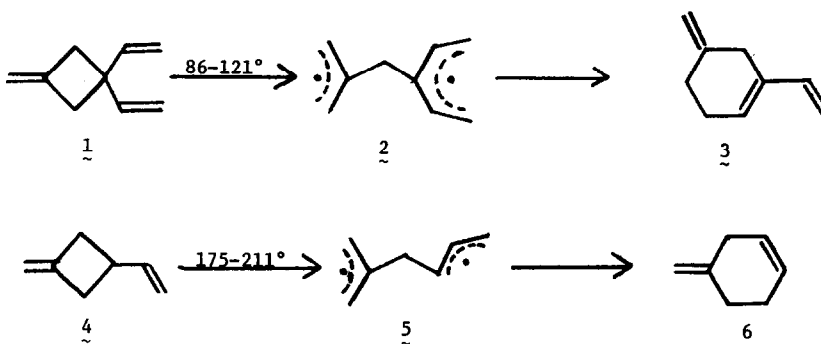


NON-CONCERTED THERMAL REORGANIZATIONS
3,3-DIVINYLMETHYLENECYCLOBUTANE

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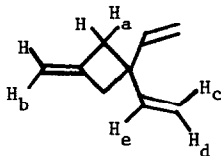
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In recent years, there have been reported a number of examples of thermal organizations of biallylic systems which, although formally appearing to be Cope rearrangements, because of structural constraints appeared to rearrange via biradical mechanisms.¹⁻⁵ Kinetic parameters^{1,2} and isotopic labelling experiments,³ or both,^{4,5} were generally utilized as mechanistic probes in these studies. We have been interested in probing potentially biradical processes using kinetic isotope effects in conjunction with rate studies.⁶ We wish to report at this time preliminary results on the thermal reorganizations of 3,3-divinylmethylenecyclobutane (1) and 3-vinylmethylenecyclobutane (4), which undergo smooth thermal conversion to products 3 and 6, respectively.



In principle, these rearrangements may proceed via two-step (biradical) mechanisms, or they may be concerted. In some systems it is possible to distinguish such extreme mechanistic types by accurate rate studies coupled with simple calculations on the thermochemical kinetics⁷ of the system. This report combines such data with kinetic isotope effect results which together we believe provide convincing evidence for the non-concerted nature of these rearrangements.

1 was synthesized via a straightforward, nine-step synthesis with the initial reaction being the thermal (2+2) cycloaddition of allene and diethyl methylenemalonate.⁸ The nmr (100MHz, CDCl₃) of 1 showed a triplet at δ 2.75 (J_{ab} =2.7 Hz) (4 H_a), a pentuplet at 4.82 (J_{ab} =2.7 Hz)(2 H_b), and a fourteen line ABX pattern for the divinyl region: δ 5.01 (J_{cd} =1.4 Hz,



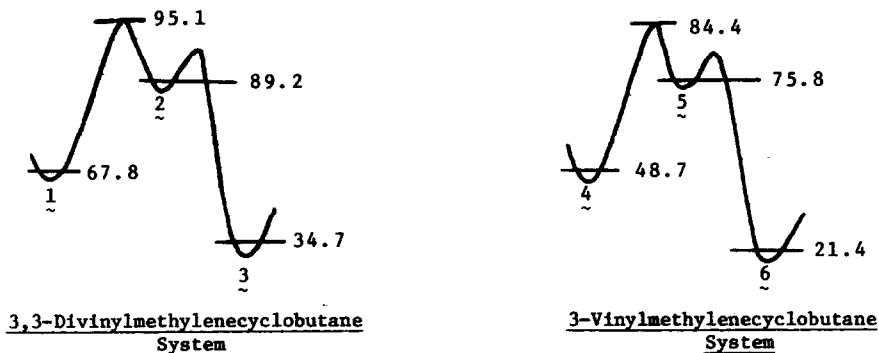
J_{ce} =16.6 Hz)(2 H_c), 5.06 (J_{cd} =1.4 Hz, J_{de} =10.2 Hz)(2 H_d) and 6.03 (J_{ce} =16.6 Hz, J_{de} =10.2 Hz) (2 H_e). 4 was synthesized via a similar, nine-step synthesis which was initiated by a thermal (2+2) cycloaddition of allene with acrylonitrile.^{9,10}

Pyrolysis experiments were carried out in n-decane solution. Rate constants were determined at seven temperatures for each molecule. Plots of $\log C_0/C$ versus time were found to be linear up to a $C_0/C > 20$, and after >8 half-lives the yields of products (by glpc) were near quantitative. Thus the reaction appears to be first order. Arrhenius plots of the data yielded good straight lines whose equations were obtained by a least squares analysis:

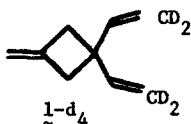
$$\text{for } \underline{1}: \log k/s^{-1} = 11.87 \pm 0.17 - 27,270 \pm 200 \text{ kcal mole}^{-1} / 2.303RT$$

$$\text{for } \underline{4}: \log k/s^{-1} = 12.70 \pm 0.19 - 35,670 \pm 410 \text{ kcal mole}^{-1} / 2.303RT$$

These activation parameters are completely compatible with the hypothesized biradical mechanisms. Compared with the activation energy for the degenerate rearrangement of methylene-cyclobutane (E_A =49.5 kcal/mole),¹¹ the first vinyl group of 4 gives rise to a lowering in E_A of about 14 kcal/mole, while the second vinyl group in 1 lowers the E_A by an additional 8 kcal/mole. These results are analogous to the comparable lowerings of 15 and 7 kcal/mole for the related series of dideuteriocyclopropane (65.1 kcal/mole),¹² vinylcyclopropane (49.7 kcal/mole),¹³ and 1,1-divinylcyclopropane (42.3 kcal/mole).¹⁴ No concerted pathways have been seriously hypothesized for the latter series of reactions. If standard heats of formation for the starting materials, potential biradical intermediates, 2 and 5, and products are calculated,^{7,15} and two-step potential energy diagrams constructed,¹⁶ the data is found to conform very nicely with expectations for the non-concerted pathways:



To further substantiate this mechanistic hypothesis, the intermolecular isotope effect for the rearrangement of 1 was determined utilizing 1-d₄.



$$k_H/k_D = 1.05 \pm 0.03 \text{ (at } 100^\circ\text{)}$$

$$k_H/k_D = 1.04 \pm 0.03 \text{ (at } 121^\circ\text{)}$$

These isotope effects, which are direct ratios of rate constants for 1 and 1-d₄, speak strongly against any σ bond formation occurring during the rate determining step. Similar studies for an actual Cope rearrangement led to the expected inverse effect.¹⁷ In fact, there have been reported no examples of rate-determining $sp^2 \rightarrow sp^3$ conversions in which the secondary deuterium isotope effects have not been inverse. The conclusion that one is forced to accept is that no rehybridization occurs during rate-determining carbon-carbon bond cleavage and that bond formation occurs in a subsequent, rapid step. Certainly a concerted mechanism is not consistent with these results.

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References and Footnotes

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