The Thermal Isomerization of Bicyclo[2,1,1]hex-2-ene

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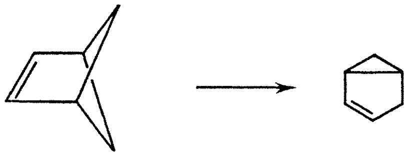
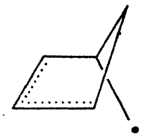
Summary The thermal isomerization of bicyclo[2,1,1]-hex-2-ene to bicyclo[3,1,0]hex-2-ene is shown to be a concerted process.

WE have studied the thermal isomerization of bicyclo-[2,1,1]hex-2-ene to bicyclo[3,1,0]hex-2-ene. In the gas phase, in an aged Pyrex reaction vessel, the isomerization is quantitative, and the process is homogeneous and kinetically first order. It is almost certainly unimolecular. In the temperature range 149—190° the rate constants fit the Arrhenius equation $k = 10^{13\cdot95+0\cdot07} \exp(-35{,}170 \pm 140 \text{ cal.}/\boldsymbol{R}T)$ sec.$^{-1}$. (Error limits are standard deviations obtained from the usual least-squares method.) Two reasonable mechanisms may be suggested for this isomerization, one involving the intermediate formation of an allylically stabilized biradical, viz,





which may internally rotate and recyclise to the product, and the other a concerted process involving simultaneous bond breaking and bond formation. On the basis of the biradical mechanism we may readily estimate the entropies of the complex and hence the "*A*" factor of the reaction. Such a calculation yields a value of $10^{14\cdot8}$ sec.$^{-1}$ with an estimated uncertainty of a factor of 2. The discrepancy between the experimental and calculated values appears well outside the combined probable errors, and would appear to rule out the biradical mechanism. For a concerted process it is unlikely that there would be any appreciable entropy change in going from reactant to transition complex, and on this assumption ($\Delta S^{\ddagger} = 0$) and noting the path degeneracy of 4 we would expect an *A* factor of $10^{14\cdot0}$. The almost exact agreement with experiment must be regarded as fortuitous, but nevertheless the results do strongly support the concerted mechanism. It should be noted that on the basis of orbital symmetry correlations such a process will only be allowed if inversion occurs at the migrating centre. This point should be experimentally verifiable with an appropriately substituted derivative.

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The recently published note of Roth and Friedrich,[1] published after this manuscript was written, supports the conclusion that this isomerization is concerted.

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W. R. Roth and A. Friedrich, *Tetrahedron Letters*, 1969, 2607.