

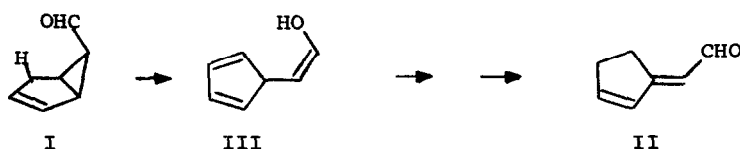
COMPETITIVE SIGMATROPIC HYDROGEN SHIFTS IN BICYCLO[3.1.0]HEX-2-EN-ENDO-6-CARBOXALDEHYDES

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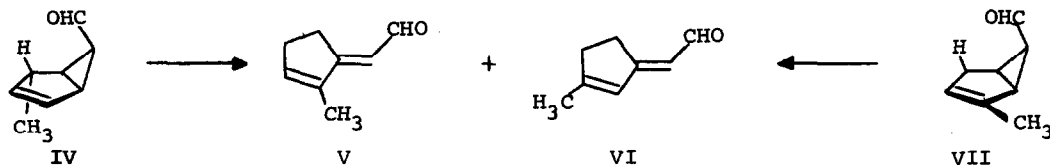
It has been reported that bicyclo[3.1.0]hex-2-en-endo-6-carboxaldehyde (I) on heating rearranges into its isomer II.¹ On the basis of numerous precedents,² the rate-determining step of this rearrangement was assumed to be a suprafacial homo-[1,5] hydrogen shift, I→III, which can be described as a $(\sigma_S^4 + \pi_S^2)$ process.³



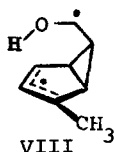
However, data in the literature suggest that systems possessing the potential for competitive thermal sigmatropic migrations of order $[i,j]$ favor rearrangement by the higher order pathway;⁴ furthermore, ΔH^\ddagger for the thermal $[1,7]$ hydrogen shift,^{4,5} is less than that for the corresponding $[1,5]$ process.² Another mode of isomerization of I therefore merits consideration. This alternate mode would involve the π -electrons of the carbon-carbon double bond and the σ -electrons between C-5 and C-6, thereby resulting in a homo-[1,7] hydrogen migration, a $(\sigma_S^4 + \pi_S^2 + \pi_A^2)$ process. Examination of a model of I suggests, moreover, that this substrate is particularly well-suited to permit evaluation of factors controlling competition between sigmatropic rearrangements. The molecular geometries of the transition states for the homo-[1,5] and homo-[1,7] hydrogen shifts in I appear to be essentially identical, if one makes the reasonable assumption that the hydrogen atoms attached to C-6 and C-7 are eclipsed, or nearly so, in the transition state for hydrogen transfer from C-4.

To obtain direct structural evidence for the hypothesized homo-[1,7] hydrogen shift, an investigation was undertaken of the thermal isomerization of the bicyclic aldehyde IV, which bears a C-4 methyl group that serves as a label of the carbon skeleton.⁶ Thermolysis

of IV at 130° afforded, in 90% yield, a mixture of V (91%) and VI (9%);⁶ a rearrangement conducted at 160° produced V and VI in the ratio 88:12. Control experiments showed the products to be stable under the conditions of the reaction.



Although a reasonable mechanism for formation of a mixture of V and VI could involve establishment of a pre-equilibrium between IV and VII, possibly promoted by the carbonyl function, followed by a rate-determining homo-[1,5] hydrogen shift, we can exclude this possibility. To accomplish this, the aldehyde VII was synthesized and thermally rearranged at 130°. Again both V and VI were formed, but in the markedly different ratio of 18:82. This result is clearly inconsistent with a pre-equilibrium and, significantly, precludes the intervention of a common intermediate, *e.g.*, VIII, in the ring-opening reactions as well.



The observations are in accord with a mechanism in which a combination of homo-[1,5] and homo-[1,7] hydrogen shifts is involved, with the latter being favored kinetically. Although the preference could conceivably arise solely from a difference in frequency factors for the two processes, the response of the reaction to increased temperature suggests that the energy of activation for the homo-[1,7] process is somewhat lower than that for the homo-[1,5] transfer.

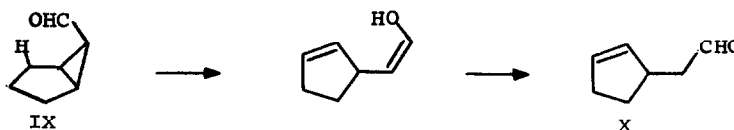
Some support for this conclusion is available from comparison of kinetic parameters for the rearrangement of I and of its dihydro analog IX⁷ which thermally rearranges to X.⁸ The results are given in Table I.⁹ The differences in the kinetic parameters of I and IX are

Table I. Rate Constants and Activation Parameters of the Isomerizations, I→II and IX→X^a

Reaction	$k_{130^\circ}(\text{sec}^{-1})$	$\log A$	$E(\text{kcal/mol})$	$\Delta H^\ddagger(\text{kcal/mol})$	$\Delta S^\ddagger(\text{e.u.})$
I→II	8.24×10^{-5}	11.7 ± 0.1	29.3 ± 0.2	28.3 ± 0.2	-12 ± 1
IX→X	4.68×10^{-5}	11.4 ± 0.1	29.5 ± 0.2	28.7 ± 0.3	-14 ± 1

^aThe isomerizations were carried out by the sealed ampoule technique using 5% v/v solutions in cyclohexane, containing 2% of an internal standard (t-butylbenzene with I, p-ethyltoluene with IX), at four temperatures between 120 and 140°C in the case of I and at five temperatures between 124.9 and 150°C for IX. The disappearance of starting material was followed by glpc. No intermediates were detected during the kinetic runs.

seen to be quite small, and without supplementary information no conclusions can unambiguously be drawn as to their origin. However knowledge of the high preference for the homo-[1,7]



hydrogen shift in IV and VII and therefore, by analogy, in I permits assignment of some meaning to the kinetic measurements, *i.e.*, the ratio of $2k_I/k_{IX}$ essentially represents the competition between homo-[1,7] and homo-[1,5] processes; the derived value of 3.6 is thus in general accord with the ratios of products observed from IV and VII.¹⁰

Given the anticipated geometrical similarity of the transition states for the two processes, the preference for the homo-[1,7] shift then may reflect the lower energy of a homotrienylyl *vs.* a homodienyl radical, although the difference, as defined by the observed ratios of V and VI, is much smaller than between a trienylyl and a dienylyl radical.^{2,5} Alternative explanations involving consideration of steric factors have been evaluated; it is our feeling that such factors play, at best, a minor role in defining the relative rates of competing sigmatropic reactions in the bicyclo[3.1.0]hex-2-en-*endo*-6-carboxaldehyde system and that orbital energies are of primary importance.¹¹

References and Footnotes

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c) H. Heimgartner, H.-J. Hansen, and H. Schmid, Helv. Chim. Acta, 53, 173 (1970).
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6. All new compounds gave analytical and spectral data consistent with the structures proposed; authentic samples of the rearrangement products were prepared. Details of these syntheses, as well as those of the bicyclic aldehydes, will be reported in a full paper.
7. IX has also been synthesized and rearranged to X by D. L. Garin, J. Org. Chem., 35, 2830 (1970); however, no kinetics were reported by this author.
8. R. K. Hill and A. G. Edwards, Tetrahedron Letters, 1964, 3239.
9. Since our first communication¹ further work has shown that the first order rate constant of I is concentration dependent. As our earlier technique required relatively high concentrations (the reaction was followed by NMR) and did not permit us to prepare samples of exactly the same initial concentration, the former values given for the activation parameters of I are not reliable. Data in Table I have been obtained using improved methods, which have enabled us to work in all cases with the same initial concentration. The concentration dependence appears to be a medium effect: Rate enhancements can also be induced by adding cyclopentanone to the samples. A similar medium effect, has been observed for a Claisen rearrangement (H. M. Frey and D. C. Montague, Trans. Faraday Soc., 64, 2369 (1968)).
10. The value of 3.6 is considered to be a lower limit for the ratio of rate constants of the homo-[1,7] and homo-[1,5] hydrogen shifts in I since the rate of the homo-[1,5] hydrogen shift in IX must be enhanced by relief of torsional strain.
11. Support of the Robert A. Welch Foundation is gratefully acknowledged. We thank the National Institutes of Health for the award of a Traineeship to one of us (KRS).