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THE THERMAL REARRANGEMENT OF *ENDO*-7-METHYL-*EXO*-7-VINYLBICYCLO[3.2.0]HEPT-2-ENE

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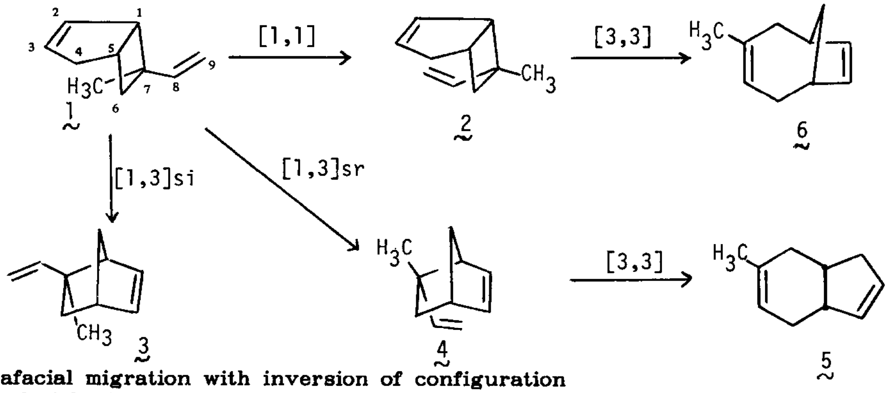
Summary: Gas-phase thermolysis of the title compound in the temperature range of 150°-166°C yields predominantly *cis*-6-methyl-4,7,8,9-tetrahydroindene by tandem [1,3]-[3,3] sigmatropic shifts; however, we cannot exclude some direct conversion by an alternative [1,3] sigmatropic migration.

We have recently reported that heating *endo*-7-methyl-*exo*-7-vinylbicyclo[3.2.0]hept-2-ene (*1*) affords predominantly *cis*-6-methyl-4,7,8,9-tetrahydroindene (*5*).[1] However, we now wish to provide a more complete profile of the energy surface of this thermal rearrangement, which we have thoroughly studied in the gas-phase[2] in the temperature range of 150°-166°C. Our investigation has confirmed that the major rearrangement product *5* is formed *via* the intermediacy of *exo*-5-methyl-*endo*-5-vinylbicyclo[2.2.1]hept-2-ene (*4*), since we observe a rapid increase followed by a gradual decrease in the amount of *4* with time in the pyrolysis mixture. Furthermore, we have determined that *1* is also converted to two minor products, *endo*-5-methyl-*exo*-5-vinylbicyclo[2.2.1]hept-2-ene (*3*) and 3-methylbicyclo[4.2.1]nona-3,7-diene (*6*), which we suspect is formed indirectly from *1* *via* the intermediacy of *exo*-7-methyl-*endo*-7-vinylbicyclo[3.2.0]hept-2-ene (*2*).[3] The full kinetic system is depicted in Scheme I, and the corresponding experimental rate constants[4] are reported in Table 1. All of these interconversions proceed by irreversible first-order kinetics.[5]



si = suprafacial migration with inversion of configuration
sr = suprafacial migration with retention of configuration

Scheme I

The structure proof for each of the rearrangement products has been based on independent synthesis except for *5*, which has been characterized by spectroscopic analysis of a preparative pyrolysis sample.[1] The epimeric mixture of *3* and *4* was prepared as previously reported,[6] and the assignments were based on the prior observation that *3* is thermally stable in this temperature range whereas *4* rearranges to *5*. Compound *6* was prepared from 3-methylbicyclo[4.2.1]nona-3,7-dien-2-one[7] by Wolff-Kishner reduction of the corresponding hydrazone.[8] Finally, epimers *1* and *2* have been differentiated using spectroscopic arguments outlined earlier.[9]

Table 1: First-order Rate Constants (k x 10^5 s)

	k_{12}	k_{13}	k_{14}	k_{45}	k_{26}
150.0°C	0.032	0.032	0.892	2.52	244
158.0°C	0.076	0.076	2.07	5.3	510
166.0°C	0.16	0.16	4.53	10.9	626

We have obtained *1* epimerically-pure by using a $AgNO_3$-doped silica gel column[10]; however, since epimer *2* was never recovered from the column, k_{26} was obtained by pyrolyzing an epimeric mixture of *1* and *2*. By also heating the epimeric mixture in the lower temperature range of 90°-100°C, we have shown that the *2*-to-*6* conversion is clean.

Our mechanistic conclusions are based on the activation parameters reported in Table 2. We believe that *6* is produced indirectly from *1*, although we do not detect any *2*.[3] The activation parameters for both [3,3]-sigmatropic rearrangements clearly support their assignment as concerted reactions, although this is certainly more convincing for the *2*-*6* than for the *4*-*5* conversion. Whereas our activation parameters for the *2*-*6* conversion are in good agreement with those reported by Hammond and DeBoer[11] for the transformation of *cis*-1,2-divinylcyclobutane to 1,5-cyclooctadiene, our values for the *4*-*5* conversion are similar to but not identical with those previously reported by Ploss[6] for the same bicyclo[2.2.1] system.

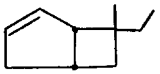
Table 2: Activation Parameters

	$\Delta H^{\ddagger}$(kcal/mole)	$\Delta S^{\ddagger}$(e.u.)
1 → *4*	36.7(±.3)	+3.9(±.7)
4 → *5*	32.9(±.2)	-2.8(±.4)
2 → *6*	21(±7)	-22(±16)

However, a mechanistic analysis of the competitive [1,1] and [1,3] shifts is more enigmatic. Our si/sr ratio of 0.04 for the [1,3]-sigmatropic migrations is comparable to the ratio of 0.14 observed by Berson[12] for the rearrangement of *endo*-6-acetoxy-*endo*-7-methylbicyclo-[3.2.0]hept-2-ene. Berson has already accounted for the predominance of the symmetry-forbidden pathway by invoking a "subjacent molecular orbital effect" analysis.[13] This similarity in si/sr ratios is good considering that Berson's system was plagued by two serious side reactions that occurred at the higher reaction temperatures: (1) Diels-Alder cycloreversion of the bicyclo[2.2.1] products and (2) [1,5]-hydrogen shift of the *endo*-methyl hydrogens. In contrast to Berson's results, however, in which epimerization (formally a [1,1] shift) proceeds almost as fast as the [1,3]sr migration, epimerization in our system represents only a minor rearrangement pathway. In yet another study of *trans*-1,2-divinylcyclobutane,[11,14] epimerization appears to compete favorably with the [1,3] migrations. Therefore, our case is the first related to the *trans*-1,2-divinylcyclobutane parent in which epimerization is not competitive with [1,3] migration.

While Berson's interpretation is that an *endo*-methyl substituent in a bicyclo[3.2.0] compound produces a "steric blockade" to the symmetry-allowed [1,3]si pathway, thus favoring another "concerted" although symmetry-forbidden pathway, [1,3]sr,[13] the enthalpy of activation for the transformation of *1* to *4* falls 9.5 kcal/mole below that reported by Berson for *endo*-6-acetoxy-*exo*-7-methylbicyclo[3.2.0]hept-2-ene, a value similar to the 12 kcal/mole increment normally associated with allylic resonance energy in a radical species. Furthermore, the value for the entropy of activation is consistent with that predicted by Benson's additivity calculations[15] for a bisallylic diradical. Finally, we suspect that there might also exist a direct *1*-*5* pathway that we have not yet considered. Attempted Runge-Kutta analysis[16] of the raw product ratios consistently produced across the temperature range estimated values for k_{45} that were greater than the experimental value by a factor of two.

To clarify some of these mechanistic questions, we have selected 7-ethyl-7-methylbicyclo[3.2.0]hept-2-ene (*7*) and 7-methyl-7-vinylbicyclo[3.2.0]heptane (*8*) as the next target molecules for study. The former will serve to segregate the [1,1] and [1,3] manifolds without any potential for successive [3,3] shifts so that we can more closely relate the energetics of the [1,3] shift of *1* to *4* to those of the comparable process in the model. The latter model will allow us to detect the alternative [1,3] migration of C-1 to C-9, should it exist, without any interference from the normal [1,3] migration of C-7 to C-3.



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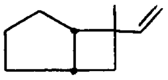

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3. We do not observe any *2* in the pyrolysis mixture, since $k_{26} >> k_{12}$. However, an examination of Dreiding models of *1* indicates that the gap between the terminal carbons of the 1,5-hexadiene moiety is 5Å, a distance too great to allow for a stereodistal Cope Rearrangement.
4. Since the ratio of *6*:*3*:*4*+*5* is invariant with time throughout the pyrolysis, we have calculated k_{12}, k_{13}, and k_{14} from the overall k for loss of 1 by partitioning this rate constant in the same proportion as the product distribution would dictate.
5. The kinetic analysis was derived from GC integrations obtained with an HP3392A integrator using an HP5890A GC in the split-mode equipped with an HP 50m x 0.2mm I.D. crosslinked methyl silicone capillary column.
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16. We are grateful to Dr. Joseph Gajewski of Indiana University for the use of his Runge-Kutta numerical integration program.

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