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THE THERMAL REARRANGEMENT OF 6-METHYL-6-VINYLBICYCLO[3.2.0]HEPTANE

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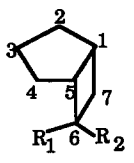
Summary: Gas-phase pyrolysis of the *endo*-vinyl epimer (**1A**) of the title compound at 275°C affords predominantly 3-(2-methyl-2-butenyl)cyclopentene (presumably the **Z** isomer), a direct [1,5]-hydrogen shift product, whereas the *exo*-vinyl epimer (**1B**) favors the fragmentation products, cyclopentene and isoprene.

We wish to report on the thermal behavior of both epimers of 6-methyl-6-vinylbicyclo[3.2.0]heptane (1),[1] which was prepared from 7-methyl-7-vinylbicyclo[3.2.0]heptan-6-one[2] *via* our standard cyclobutanone reduction.[3] We have conducted a rigorous kinetic investigation[4] of the gas-phase (275°C) pyrosylate[5] of each individual epimer of the title compound using nonane as an internal standard. The rate constant for overall loss of reactant epimer (k_d) as well as the relative distribution of products among three rearrangement modes, [1,5]-hydrogen shift ($k_{1,5}$), [1,3]-carbon migration ($k_{1,3}$), and retro-[2+2] cycloreversion or fragmentation (k_f),[6] are reported in Table 1.



1

	R_1	R_2
epimer A	$CH=CH_2$	CH_3
epimer B	CH_3	$CH=CH_2$

Surprisingly, the most favorable rearrangement mode for epimer **A** is a [1,5]-hydrogen shift, formally a retro-ene reaction, of the *endo*-hydrogen on C-4 to the methylene carbon of the *endo*-vinyl substituent. The most convincing evidence for the characterization of this product as 3-(2-methyl-2-butenyl)cyclopentene is derived from ^{13}C-NMR.[7] We attribute the greater reactivity of epimer **A** relative to epimer **B** (a factor of 16) to steric destabilization operating in epimer **A**. Epimer **A** can, therefore, undergo a facile [1,5]-hydrogen shift assisted by

Table 1. Kinetic Data for 6-methyl-6-vinylbicyclo[3.2.0]heptane (1) at 275°C.

	$k_d \times 10^5$ s	$k_{1,5}/k_d$	$k_{1,3}/k_d$	k_f/k_d
epimer **A**	26. (28.)†	.80 (.82)†	.03 (.01)†	.17
epimer **B**	1.6 (1.9)†	.08*	.22	.70

† Nonlinear least squares values, where different from linear least squares data, are given in parentheses.

* This is presumably an indirect diradical-mediated [1.5]-hydrogen shift product; its GC retention time is slightly different from that observed for epimer **A**.

the close proximity of the C-4 *endo*-hydrogen to the migration terminus.[8] Chickos and Frey have previously concluded that an analogous [1,5]-hydrogen shift in 2,2-dimethyl-1-vinylcyclobutane is concerted.[9] However,

the [1,5]-hydrogen shift is far less important in this monocyclic vinylcyclobutane with $k_{1,5}/k_d = 0.18$. The only monocyclic vinylcyclobutane that favors the [1,5]-hydrogen shift is cis-2-ethylvinylcyclobutane, for which a $k_{1,5}/k_d$ of 0.66 is observed.[10] Moreover, the *cis-trans* rate ratio of 13 for this monocyclic system is similar to the corresponding rate ratio (k_A/k_B = 16) that we have noted. The kinetic data from the related monocyclic vinylcyclobutane systems are reported in Table 2.

Although the phenomenon of *cis-trans* isomerism has complicated the kinetic analysis of other substituted vinylcyclobutanes such as 2-ethylvinylcyclobutane,[10] there is a complete absence of geometric isomerism in either epimer of compound 1. One plausible explanation for this is that the allylic diradical that is produced upon homolytic cleavage of the C-5/C-6 bond is sufficiently sterically hindered that fragmentation rather than recombination is the favored process *via* the diradical intermediate. The lack of epimerization implicates a nonequilibrated diradical intermediate.

Because epimer **B** cannot undergo a direct [1,5]-hydrogen shift, its thermal energy profile must necessarily traverse a diradical intermediate. Comparing actual rates, however, epimer **A** still fragments 4 times faster than epimer **B**. A similar analysis of 2-ethylvinylcyclobutane reveals that fragmentation is 5.5 times faster in the *cis* than in the *trans* isomer.[10] Relief of steric interactions in epimer **A** and *cis*-2-ethylvinylcyclobutane is apparently responsible for these differences.

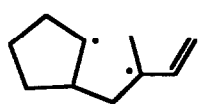
Table 2. Kinetic Data for Related Vinylcyclobutanes

	$k_d x 10^5$ s	$k_{1,5}/k_d$	$k_{1,3}/k_d$	k_f/k_d
2,2-dimethyl-vinylcyclobutane[9]	35.6 (280°C.)	0.18	0.77	0.04
cis-2-ethyl-vinylcyclobutane[10]	43.5(290°C.)	0.66	0.18	0.04[f]
trans-2-ethyl-vinylcyclobutane[10]	3.6(290°C.)	-----	0.44	0.28[f]

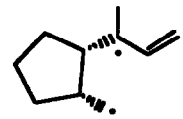
[f]The rate ratios do not sum to one due to exclusion of geometrical isomerism.

While noting that the rate constants for *cis*- and *trans*-2-ethylvinylcyclobutane are approximately twice those for epimer **A** and epimer **B**, respectively, one can readily account for this variation by the 15°C temperature difference. If anything, compound 1 might be slightly more reactive due to the greater degree of substitution at C-6 in 1 versus C-1 in 2-ethylvinylcyclobutane. Because of the greater stability of a tertiary (C-2) versus a primary (C-4) radical, 2,2-dimethylvinylcyclobutane undergoes regiospecific fragmentation. In contrast, the fragmentation mode in 2-ethylvinylcyclobutane is not as clean. Yet in compound 1 fragmentation proceeds exclusively along the C-1/C-7 and C-5/C-6 axes (an obvious entropic benefit), parallel to MS fragmentation[1]; however, the presence of three [1,3]-carbon migration products in about equal intensities (1.5: 3.3: 1) in the pyrosylate of epimer **B** indicates that both diradical intermediates 1a (C-5,C-6 cleavage) and 1b (C-6,C-7 cleavage) must form: 1a to yield both *cis*- and *trans*-3-methylbicyclo[4.3.0]non-3-ene and 1b to yield *cis*-2-methylbicyclo[4.3.0]non-2-ene. One again observes similarities with *trans*-2-ethylvinylcyclobutane, which affords two different [1,3]-carbon migration products in a 9:1 ratio resulting from a secondary, allylic and a primary, allylic diradical, respectively. However, the primary, allylic diradical is apparently more competitive in our system. Another parallel between epimer **B** and

trans-2-ethylvinylcyclobutane is the greater proportion of [1,3]-carbon migration relative to that in their respective geometric isomers.



1 a



1 b

In summary, the thermal behavior of epimers **A** and **B** parallels that of *cis*- and *trans*-2-ethylvinylcyclobutane in many respects. In particular, the dominant thermal pathway observed for both epimer **A** and *cis*-2-ethylvinylcyclobutane is a concerted [1,5]-hydrogen shift. However, geometric isomerism, significant in the monocyclic system, is absent in compound 1. The most plausible explanation for this difference is that the bicyclic system affords a nonequilibrated diradical that favors fragmentation over recombination.

REFERENCES AND NOTES

1. Epimeric separation is readily achieved by preparative GC (GowMac 69-350, 8' x 1/4" 20% Carbowax 20M column at 90°C.). **IR**(cm^{-1}), of epimeric mixture: 3040(m), 2910(s), 1615(s), 975(s), 885(s). **^{1}H-NMR** ($CDCl_3$): epimer **A**, 5.8 ppm (1H,dd), 5.0 (1H,dd), 4.9 (1H,dd), 2.8 (1H,pent), 2.3 (1H,dt), 1.7 (5H, m), 1.4 (3H,m), 1.25 (3H,s); epimer **B**, 6.1ppm (1H,dd), 5.0 (1H,dd), 4.9 (1H,dd), 2.7 (1H, pent), 2.45(1H,dt), 2.1 (1H, dt), 1.8 (3H,m), 1.3-1.4(4H,m), 0.95 (3H,s). **^{13}C-NMR** ($CDCl_3$): epimer **A**, 143.9 ppm(CH=), 111.2(CH_2=), 49.4(CH), 38.9(C), 34.4(CH_2), 32.6(CH), 32.0(CH_2), 29.8(CH_3), 28.1(CH2), 25.4(CH_2); epimer **B**, 149.8(CH=), 107.7(CH_2=), 46.4(CH), 38.3(C), 36.3(CH_2), 32.9(CH), 32.0(CH_2), 27.5(CH_2), 26.2(CH_2), 20.5 (CH_3). The shielding of the *endo* substituent by the cyclopentane ring observed by Dreiding[2] in the ^{1}H-NMR of the ketone precursors is apparent in both the ^{1}H-NMR and ^{13}C-NMR chemical shifts (relevant values are underlined). We are grateful to Julie Otter for acquiring these spectra on a Varian VXR400 at the FDA lab (Washington, D.C.). The mass spectra of both epimers, obtained with a Finnigan ion trap detector connected to a Varian 3400 GC using a J&W DB-5 column(30m x 0.25mm ID), were virtually identical. **MS** (70 eV): 136(1), 121(13), 107(10), 93(19), 79(27), 67(100). Elemental analysis of epimeric mixture: 87.63%C, 11.77%H ($C_{10}H_{16}$).
2. D.A. Jackson, M. Rey, and A.S. Dreiding, *Helv. Chim. Acta* **1983**, *66*, 2330.
   Our failed attempts to simulate the sealed tube technique prompted the development of a similar reaction in chloroform heated under vigorous reflux. Our yield of 20% under such conditions compares favorably with the 28% yield reported by Dreiding.
3. J.D. Burkey, P.A. Leber, L.S. Silverman, *Synth. Commun.***1986**, *16*, 1363.
4. 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 ID crosslinked methyl silicone capillary

column. The first-order rate plots were subjected to both linear and nonlinear (Simplex) least-squares analyses with little deviation in the resultant rate constants. By linear least-squares analysis, k_d for epimer **A** is $1.56(\pm.05) \times 10^{-2}$ min^{-1} (cc = 0.9977); k_d for epimer **B** is $9.9(\pm.2) \times 10^{-4}$ min^{-1} (cc = 0.9992). Epimer **A** was monitored for 1.5 half-lives; epimer **B**, for almost 6 half-lives.

5. J.J. Gajewski and S.K. Chou, *J. Am. Chem. Soc.* **1977**, *57*, 5696.
6. Using the column described in ref. 5 with a temperature program of 90°C for 1 min followed by a 5°C /min temperature increase to 110°C., the GC retention times were as follows: isoprene and cyclopentene, 4.9-5.0 min; cyclohexane(GC solvent), 5.2 min; nonane, 6.8 min; epimer **A**, 7.9 min; epimer **B**, 8.2 min; [1,5]-hydrogen shift product(s), 8.7-8.9 min; [1,3]-carbon shift product(s), 10.1-10.3 min.
7. A preparative tube pyrolysis of ca. 25 μl of epimer **A** afforded sufficient material to obtain a ^{13}C-NMR spectrum of the dominant product, since the fragmentation products readily evaporated upon sample preparation: 135.4 ppm (CH=), 135.1(C=), 130.1(CH=), 119.7(CH=), 44.0(CH), 37.6(CH_2), 31.9(CH_2), 29.7(CH_2), 23.7(CH_3), 13.5(CH_3). The **Z** stereochemistry is presumed from an examination of molecular models.
8. Measurement of this distance using Dreiding models provides a minimum separation of 1.3-1.4Å; using Chem 3D Plus (Cambridge Scientific Computing, Inc.) software and standard MM2 parameters for the bicyclo[3.2.0] system, the separation was determined to be 1.5Å.
9. J.S. Chickos and H.M. Frey, *J. Chem. Soc., Perkin Trans. II*, **1987**, 365.
10. Jordan, L.M., Ph.D. dissertation, Yale University, 1974; J.J. Gajewski, "Hydrocarbon Thermal Isomerizations," Academic Press, NY, 1981, pp. 178.

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