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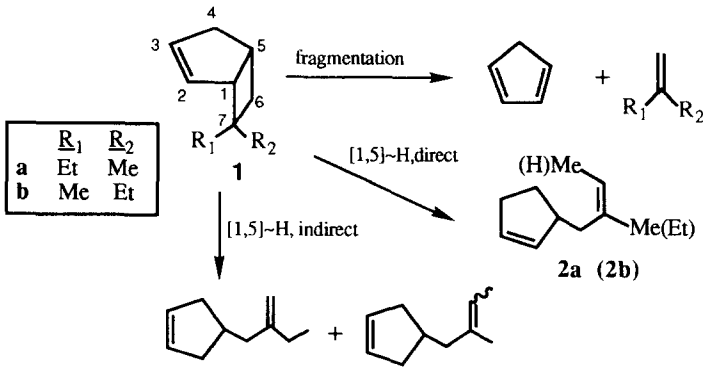
The Thermal Rearrangement of 7-Ethyl-7-methylbicyclo[3.2.0]hept-2-ene (1)

Timothy E. Glass, David M. Goldstein, and Phyllis A. Leber*

Department of Chemistry, Franklin & Marshall College, P.O. Box 3003, Lancaster, PA 17604-3003 (USA)

Abstract: The title compound **1**, when subjected to gas-phase pyrolysis at 275°C, undergoes predominantly fragmentation to cyclopentadiene and 2-methyl-1-butene.

We wish to report on the thermal behavior of 7-ethyl-7-methylbicyclo[3.2.0]hept-2-ene (**1**),[1] which was prepared from 7-ethyl-7-methylbicyclo[3.2.0]hept-2-en-6-one[2] *via* our standard cyclobutanone reduction[3] in typical yield. Because all attempts at epimeric separation of compound **1** have proven futile when **1** was prepared by low-temperature Wolff-Kishner reduction of the ketene cycloadduct of cyclopentadiene and ethyl methyl ketene, we have synthesized each separate epimer of **1** (**1a** and **1b**, see Scheme 1) from the corresponding ketone diastereomer.[2] We have conducted a rigorous kinetic investigation[4] of the gas-phase (275°C.) pyrosylate[5] of the title compound using nonane as an internal standard. The rate constant for overall loss of **1** (k_d) as well as the relative distribution of products among three rearrangement modes (see Scheme 1), direct [1,5]-hydrogen shift ($k_{1,5}$), indirect [1,5]-hydrogen shift ($k_{1,5'}$), and retro-[2+2] cycloreversion or fragmentation (k_f),[6,7] are reported in Table 1.



	R_1	R_2
a	Et	Me
b	Me	Et

Scheme 1. Thermal rearrangement of **1**

The most favorable rearrangement mode for compound **1** is regiospecific fragmentation to 2-methyl-1-butene and cyclopentadiene. However, two [1,5]-hydrogen shifts also occur. The direct [1,5]-hydrogen shift, formally a retro-ene reaction, involves migration of a hydrogen from the *endo*-ethyl methylene (in **1a**) or from the *endo*-methyl (in **1b**) on C_7 to C_3 with concurrent migration of the pi bond and cleavage of the sigma bond between C_1 and C_7 to form **2a** and **2b**, respectively. The indirect [1,5]-hydrogen shift we attribute to a diradical-mediated process involving homolysis of the sigma bond between C_1 and C_7 followed by a hydrogen shift from a methyl or methylene on C_7 to C_1. The formation of only one of the two possible indirect [1,5]-hydrogen shift products from either **1a** or **1b**, a different 1,5' product in each case,[8] suggests that the resultant diradical is not equilibrated, which we attribute to steric hindrance to rotation about the bond between C_6 and C_7 while the rotating arm is close enough to the five-membered ring to yield rearrangement rather than fragmentation.

Table 1. Kinetic Data for **1a** and **1b** at 275°C.

	$k_d x 10^5$ s	$k_{1,5}/k_d$	$k_{1,5'}/k_d$ §	k_f/k_d
compound **1a**	2.0 (2.3)†	0.16	< 0.02	0.82
compound **1b**	1.6 (2.0)†	0.25	< 0.01	0.74

† 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.

Kinetic data from disubstituted vinylcyclobutane systems related to compound **1** are reported in Table 2. Chickos and Frey have previously concluded that a [1,5]-hydrogen shift in 2,2-dimethylvinylcyclobutane analogous to the direct [1,5]-hydrogen shift in **1** is concerted.[9] The fact that **1a** yields **2a**[10] exclusively whereas **1b** affords only **2b** is consistent with a concerted process. However, the distance between the migrating hydrogen and the carbon terminus in the bicyclic compounds (compound **1**, Table 1 and 7,7-dimethylbicyclo[3.2.0]hept-2-ene,[11] Table 2) is roughly 1 Å greater than in substituted monocyclic vinylcyclobutanes such as 2,2-dimethylvinylcyclobutane (Table 2). An alternative explanation for the different direct [1,5]-hydrogen shift products obtained from **1a** and **1b** is that a short-lived biradical generated *via* C_1-C_7 bond cleavage collapses to form the [1,5]-hydrogen shift product while the *endo*-substituent R_1 resides in the vicinity of the allylic radical unit. This interpretation is similar to Gajewski's rationalization of preferential (although not exclusive) deuterium migration in *syn*-7-(trideuteriomethyl)-α-pinene involving the intermediacy of a nonequilibrated diradical species.[12] It also links the direct and indirect [1,5]-hydrogen shift products that result from either **1a** or **1b** to the same intermediate, separated only by the extent of bond rotation, a function of the discrete lifetime of the species.

Table 2. Kinetic Data for Related Disubstituted Vinylcyclobutanes at 275°C

	$k_d x 10^5$ s	$k_{1,5}/k_d$	$k_{1,5'}/k_d$	k_f/k_d
2,2-Me_2-vinylcyclobutane[9]	16.5	0.21	0.01	0.73
7,7-Me_2-bicyclo[3.2.0]hept-2-ene[11]	1.75	0.15	< 0.01	0.84

The dominance of fragmentation can also be accounted for by the formation of a diradical intermediate. Although fragmentation can proceed either directly *via* [2+2]-cycloreversion or indirectly *via* the intermediacy of 5-ethyl-5-methylnorbornene,[13] which can then undergo a successive retro-Diels-Alder reaction, we have observed none of the product that would result from [1,3]-carbon migration.[14] From the GC detection limits, we extrapolate that the [1,3]-carbon shift can at most represent only 10% of the total fragmentation pathway.

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 fragmention.[1] The observation of regiospecific fragmentation, in contrast to the report by Cocks and Frey[15] for bicyclo[3.2.0]hept-2-ene, the parent system, of competition from cleavage along the C_1-C_5 and C_6-C_7 axes, is consistent with a diradical intermediate that is stabilized by an allyl unit and a tertiary center at C_7. The large k_f/k_d ratios (see Tables 1 and 2) can also be rationalized on the basis of diradical intermediate stability.

The lack of epimerization, formally a [1,1]-sigmatropic rearrangement, between **1a** and **1b** also implicates a nonequilibrated diradical intermediate. In contrast, a number of related monocyclic vinylcyclobutanes undergo facile epimerization (see Table 3), presumably *via* a diradical intermediate. Reclosure to the vinylcyclobutane is apparently sterically prohibited in **1a** and **1b**.

Table 3. Kinetic Data for Related Monocyclic Vinylcyclobutanes at 290°C

	$k_d x 10^5$ s	$k_{1,1}/k_d$	$k_{1,5}/k_d$	k_f/k_d
cis-2-ethylvinylcyclobutane[16]	47.	0.13	0.66	0.18
cis-2-Me-1-*trans*-propenylcyclobutane[16]	20.	0.30	0.27	0.36
cis-2-Me-1-*cis*-propenylcyclobutane[16]	15.	0.37	0.03	0.57
cis-2-(1-MeO-ethyl)vinylcyclobutane[17]	23.*	0.35	0.20	0.35

*Rate constant at 290°C was calculated using the Arrhenius parameters provided by the authors.

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REFERENCES AND NOTES

1. Characterization of **1a** is as follows: **IR**(cm^{-1}): 3049(m), 2959(s), 714(m). **^{1}H-NMR** ($CDCl_3$): 5.9 ppm(2H), 1.4(3H); the methyl singlet and the olefinic hydrogens were the only distinguishable features in the non-first-order spectrum. **^{13}C-NMR** ($CDCl_3$): 132.0(CH=), 131.4(CH=), 55.4(CH), 42.1(C), 39.6(CH_2), 39.5(CH_2), 30.1(CH_2), 29.9(CH), 26.0(CH_3), 8.4(CH_3). **MS** (70 eV): 136(1), 107(3), 91(7), 79(13), 66(100). Elemental analysis: 87.88%C, 11.84%H ($C_{10}H_{16}$). Characterization of **1b** is as follows: **IR**(cm^{-1}): 3049(m), 2959(s), 1605(w), 713(m). **^{1}H-NMR** ($CDCl_3$): 5.8 ppm(dt,1H), 5.7(dd,1H), 2.9(br s,1H), 2.7(p,1H), 2.5(dd,1H), 2.1(d,1H), 1.9(dd,1H), 1.55(q,2H), 1.3(dd,1H), 0.9(t,3H), 0.8(s,3H); this spectrum was acquired by Julie Otter on a Varian VXR400 at the FDA Lab

(Washington, DC). ^{13}C-NMR ($CDCl_3$): 132.0(CH=), 131.5(CH=), 54.6(CH), 42.6(C), 39.9(CH_2), 39.1(CH_2), 35.0(CH_2), 30.4(CH), 21.1(CH_3), 8.8(CH_3). Elemental analysis: 87.97%C, 11.81%H ($C_{10}H_{16}$). The shielding of the *endo* substituent by the cyclopentene ring observed[2] in the ^{13}C-NMR of the ketone precursors is apparent in both the ^{1}H-NMR and ^{13}C-NMR chemical shifts (relevant values are underlined). 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.

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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 **1a** is 1.22(±.01) x 10^{-3} min^{-1} (cc = 0.9997); **1b**, 9.6(±0.1) x 10^{-4} min^{-1}. Compound **1a** was monitored for more than 7 half-lives; **1b**, almost 4 half-lives.
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6. Using the column described in ref. 4 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: 2-methyl-1-butene and cyclopentadiene, 4.8-5.0 min; cyclohexane(GC solvent), 5.2 min; nonane (internal standard), 6.8 min; compound **1**, 7.9-8.0 min; [1,5]-hydrogen shift products, 8.3-8.7 min.
7. Given that each reactant **1** partitions itself among three parallel first-order reactions, the product concentration ratios are invariant with time. Thus, by employing an internal GC standard in the pyrolysis sample, k_f was derived from the difference between k_d and ($k_{1,5}$ + $k_{1,5}$') because rate constant ratios are determined by measuring product concentration ratios.
8. For **1b** the amount of the 1,5' product relative to the 1,5 product is 3%, a value comparable to that observed in 2,2-dimethylvinylcyclobutane.[9] For **1a**, however, the amount of indirect [1,5]-hydrogen shift product is approximately 10% of the direct [1,5]-hydrogen shift product.
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10. The identity of **2a** was confirmed by GC coinjection of the [1,5]-hydrogen shift product of *exo*-6-methyl-*endo*-6-vinylbicyclo[3.2.0]heptane[18] with **1a** pyrosylate. There is a GC peak at 8.5 min that we attribute to a Cope Rearrangement product of **2a**; the Cope Rearrangement of **2b**, however, is degenerate.
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12. Gajewski, J.J.; Hawkins, C.M. *J. Am. Chem. Soc.* **1986**, *108*, 838.
13. 5-Ethyl-5-methylnorbornene was synthesized independently by Wolff-Kishner reduction at 40°C. of the hydrazone derivative of 5-acetyl-5-methylnorbornene, the Diels-Alder cycloadduct of cyclopentadiene and 3-methyl-3-buten-2-one (CTC Organics). The overall yield from 3-methyl-3-buten-2-one (freshly distilled just prior to use) was 5%. The product mixture consisted of a .85: .15 ratio of the two epimers. **^{13}C-NMR** ($CDCl_3$) of the major epimer (probably *exo*-ethyl, *endo*-methyl): 136.2ppm(CH=), 136.0(CH=), 50.6(CH), 47.9(CH_2), 43.3(CH), 41.5 (C), 40.1(CH_2), 35.3(CH_2), 23.9(CH_3), 9.8(CH_3).
14. Because GC retention times for the [3.2.0] and [2.2.1] compounds were similar on the column used for the kinetic analysis (see reference 4), the absence of any [1,3]-carbon shift product at the GC detection limit was verified using a combined J&W DB-5 column (30m x 0.25mmID) and HP Carbowax 20M column (25m x 0.2mm ID) joined with a Press-fit™ connection (ICT 0.25/0.25mm).
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