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The Thermal Rearrangement of 7,7-Dimethylbicyclo[3.2.0]hept-2-ene

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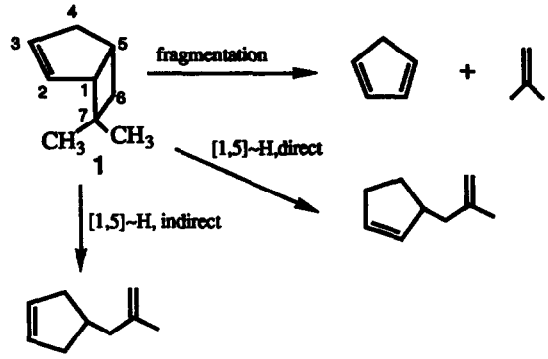
Abstract: The title compound, when subjected to gas-phase pyrolysis at 275°C, undergoes predominantly fragmentation to cyclopentadiene and isobutylene.

We wish to report on the thermal behavior of 7,7-dimethylbicyclo[3.2.0]hept-2-ene (**1**),[1] which was prepared from 7,7-dimethylbicyclo[3.2.0]hept-2-en-6-one[2] *via* our standard cyclobutanone reduction[3] in an overall yield of 12% based on the ketene precursor isobutyryl chloride. We have conducted a rigorous kinetic investigation[4] of the gas-phase (275°C.) pyrosylate[5] of the title compound using methylcyclohexane 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] are reported in Table 1.



Scheme 1. Thermal rearrangement of **1**

The most favorable rearrangement mode for compound **1** is fragmentation to isobutylene 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*-methyl 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. 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 on C-7 to C-1.

Table 1. Kinetic Data for 7,7-dimethylbicyclo[3.2.0]hept-2-ene (1) at 275°C.

	$k_d x 10^5$ s	$k_{1,5}/k_d$	$k_{1,5'}/k_d$[§]	k_f/k_d
compound 1	1.75 (1.72)[†]	.15	<.01	.84

[†] 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 (6.64 min) is slightly different from that (6.82 min) observed for the direct [1,5]-hydrogen shift product. The two positional isomers are virtually identical structurally.

Kinetic data from 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.[7] Interestingly, the relative contribution of the direct [1,5]-hydrogen shift is comparable in both the monocyclic 2,2-dimethylvinylcyclobutane system and in the bicyclic system (compound 1). Similarly, the diradical-mediated [1,5]-hydrogen shift in each system is relatively inconsequential with $k_{1,5}/k_d \approx .01$.

Table 2. Kinetic Data for Related Vinylcyclobutanes at 275°C[f]

	$k_d x 10^5$ s	$k_{1,5}/k_d$	$k_{1,3}/k_d$	k_f/k_d
α-pinene[12]	190	0.47	0.16	0.37
2,2-dimethylvinylcyclobutane[7]	15.5	0.18	0.04	0.77
bicyclo[3.2.0]hept-2-ene[10]	0.92	---	[0.44]*	[0.43]*

[f] Rate constants at 275°C have been calculated using the Arrhenius parameters provided by the authors.
* Ratios extrapolated from graphical estimate of $k_{1,3}$ based on the concentration of norbornene.

The dominance of fragmentation can 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 5,5-dimethylnorbornene, 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. From the GC detection limits, we can extrapolate that the [1,3]-carbon shift can at most represent only 10% of the total fragmentation pathway.

Gajewski has attributed the ratio of rearrangement to cleavage in vinylcyclobutane thermolyses to "the geometry of the species generated upon initial fission of the cyclobutane allylic bond." [8] However, the diradical species derived from compound 1 and from bicyclo[3.2.0]hept-2-ene would be identical geometrically except for the degree of substitution at C-7. Thus, this argument cannot account for the considerable difference in the rearrangement:cleavage ratio of approximately 0 for compound 1 as compared to 1 for the parent system.[9]

Because a [1,3]-carbon shift was estimated by Cocks and Frey to constitute half of the fragmentation manifold in bicyclo[3.2.0]hept-2-ene,[10] there is a clear departure between the unsubstituted and the disubstituted bicyclic vinylcyclobutanes. We believe that a diradical intermediate can account for both fragmentation pathways: the direct [2+2]-cycloreversion and the tandem [1,3]-carbon shift--[4+2]-cycloreversion. When the nonallylic radical center is tertiary rather than primary, the longer-lived intermediate favors fragmentation over reclosure. 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 for 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.

A kinetic comparison of compound **1** with 2,2-dimethylvinylcyclobutane shows overall rearrangement occurring one order of magnitude faster in the monocyclic system, suggesting that the diradical intermediate forms less readily from the bicyclic compound **1**. We attribute this to the resistance of C-1 to developing radical character because in every other respect the two diradical intermediates should have comparable stability. It is also noteworthy that vinylcyclobutane[11] and bicyclo[3.2.0]hept-2-ene[10] have very comparable overall rates of decomposition. Because bicyclo[3.2.0]hept-2-ene has a second cleavage mode due to nonregiospecific fragmentation, this compensates for the reduced reactivity inherent in the bicyclic system. However, regiospecific fragmentation deprives compound **1** of a second fragmentation manifold.

If both the [1,3]-carbon shift and fragmentation pathways traverse a diradical intermediate, the sum of these two rearrangement modes is relatively invariant (.84 for compound **1**, .81 for 2,2-dimethylvinylcyclobutane, and .87 for bicyclo[3.2.0]hept-2-ene) except for α-pinene (.53).[12] Alpha-pinene must not afford an equilibrated diradical because, if it did, the diradical would be very similar structurally to that derived from compound **1**. One would thus expect greater similarity in rearrangment product distributions between the two compounds. An examination of Dreiding models reveals that the C-3 to *endo*-methyl H distance is virtually identical in both compound **1** and in α-pinene at 2.3Å. Therefore, the greater proportion of the concerted [1,5]-hydrogen shift product must be attributable to some other factor such as the greater ring strain in α-pinene, which might enhance this rearrangement mode by increasing the inward rotational component of the cyclobutane ring opening.

Table 3. Effect of Dimethyl Substitution on $k_{1,3}/k_f$ Ratio at 275°C*

	$k_{1,3}/k_f$		$k_{1,3}/k_f$
vinylcyclobutane[11]	0.67	2,2-dimethylvinylcyclobutane[7]	0.05
bicyclo[3.2.0]hept-2-ene	1.0[10] (2.1)[9]	compound **1**	~0
bicyclo[3.1.1]hept-2-ene[13]	5.1	α-pinene[12]	0.43

*Rate constants at 275°C have been calculated using the Arrhenius parameters provided by the authors.

The diminution in the $k_{1,3}/k_f$ ratio by roughly a factor of ten on 2,2-dimethyl substitution of vinylcyclobutane (see Table 3) is consistent also with our observation in the bicyclo[3.2.0]hept-2-ene system and that of Gajewski in the bicyclo[3.1.1]hept-2-ene system. This trend corroborates our earlier conclusion that the vinylcyclobutane ring opening traverses a diradical intermediate.

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REFERENCES AND NOTES

1. Characterization of **1** is as follows: **IR**(cm^{-1}): 3000(m), 2905(s), 1585(w), 690(m). **^{1}H-NMR** ($CDCl_3$): 6.47 ppm (2H), 2.1-4.0 (6H), 1.22 (3H), 0.88 (3H). **^{13}C-NMR** ($CDCl_3$): 132.0 (CH=), 131.5 (CH=), 56.6 (CH), 40.8 (CH_2), 39.6 (CH_2), 39.0 (C), 30.3 (CH_3), 29.9 (CH), 24.7 (CH_3).The shielding of the *endo* substituent by the cyclopentene 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). **MS** (70 eV): 122(18), 107(7), 93(14), 80(52), 66(100). Elemental analysis: 87.13%C, 11.69%H (C_9H_{14}).
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