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Thermal reactions of *endo*- and *exo*-6-methylbicyclo[3.2.0]hept-2-enes: an experimental test for a potential ring inversion

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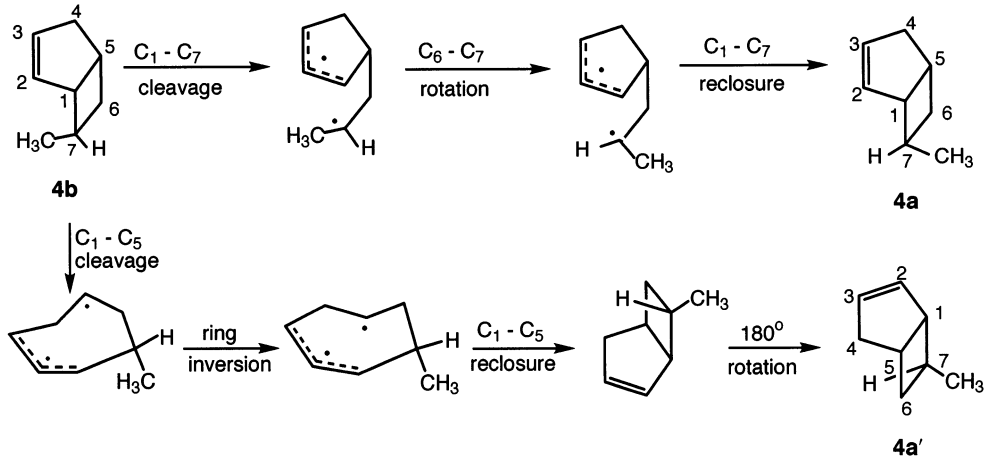
Abstract—*endo*-6-Methylbicyclo[3.2.0]hept-2-ene at 275°C in the gas phase isomerizes and fragments with a first-order rate constant for disappearance of 7.3×10^{-6} s^{-1}. The *exo*-methyl isomer is not formed; the ring inversion isomerization of the bicyclo[3.2.0]hept-2-ene is not kinetically competitive. © 2000 Elsevier Science Ltd. All rights reserved.

At 275°C in the gas phase *endo*-7-methylbicyclo[3.2.0]-hept-2-ene gives *exo*-7-methylbicyclo[3.2.0]hept-2-ene and *exo*-5-methylnorbornene at competitive rates, as well as fragmentation products (propene and cyclopentadiene). The rate constant for overall decomposition of *endo*-7-methylbicyclo[3.2.0]hept-2-ene (k_d^{endo}) is 1.15×10^{-5} s^{-1}. Similarly, *exo*-7-methylbicyclo[3.2.0]hept-2-ene ($k_d^{exo}=1.8\times10^{-5}$ s^{-1}) isomerizes to *endo*-7-methylbicyclo[3.2.0]hept-2-ene and *exo*-5-methylnorbornene.[1]

Two possible processes could well account for the equilibration of *endo*- and *exo*-7-methylbicyclo[3.2.0]hept-2-enes (Scheme 1): (1) C_1–C_7 bond cleavage with subsequent rotation about the C_6–C_7 bond followed by reclosure, or (2) C_1–C_5 bond cleavage followed by ring inversion and reclosure. Thermal one-center epimerizations of cyclobutane derivatives are well known, as are ring inversion isomerizations in bicyclic hydrocarbons such as those demonstrated for bicyclo[2.1.0]pentanes,[2,3] bicyclo[2.2.0]hexane,[4] and bicyclo[3.1.0]hex-2-enes.[5,6]



Scheme 1. Two paths rationalizing the *endo* → *exo* isomerization of *endo*-7-methylbicyclo[3.2.0]hept-2-ene.

Keywords: bicyclic aliphatic compounds; hydrocarbons; kinetics; pyrolysis; rearrangements.
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We have differentiated between these two mechanistic alternatives, as we report in this paper, by examining the thermal chemistry of the 6-methylbicyclo[3.2.0]hept-2-enes, closely-related analogs of the 7-methyl isomers studied earlier. In the 6-methyl system, reversible cleavage of the C_1–C_7 bond will not cause isomerization. Hence, an *exo–endo* interconversion of the 6-methylbicyclo[3.2.0]hept-2-enes would signal a ring inversion isomerization. Conversely, the absence of *exo–endo* interconversion for the 6-methyl isomers would strongly favor *exo–endo* equilibration of the 7-methylbicyclo[3.2.0]hept-2-enes by way of C_1–C_7 bond fission and recombination.

The title compound **1** has been prepared by selective diimide reduction of 6-methylenebicyclo[3.2.0]hept-2-ene[7] at temperatures of −20 to −30°C (Scheme 2) using anhydrous hydrazine and 30% hydrogen peroxide in excess.[8] Diimide reductions below 0°C are rare due to the enhanced propensity of diimide to disproportionate at lower temperatures;[9] in this instance low temperatures were required to achieve a significant kinetic differentiation between cyclopentene and methylenecyclobutane π bonds. The reduction afforded all three partially reduced products in a 5:3.5:1 ratio of *exo*-6-methylbicyclo[3.2.0]hept-2-ene (**1a**): *endo*-6-methylbicyclo[3.2.0]hept-2-ene (**1b**): 6-methylenebicyclo[3.2.0]-heptane (**2**). Overall, partial reduction relative to complete reduction was favored by ≈2:1. We were also able to effect partial reduction with similar results through hydrogenation of 6-methylenebicyclo[3.2.0]-hept-2-ene at −50°C with Lindlar's catalyst. The mixture of five products and unreacted starting material was readily separated by preparative GC[10] on a 2.3 m×6.4 mm 20% β,β′-oxydipropionitrile (Supelco)/60–80 mesh Chromosorb P-NAW column operating at 53°C. Full characterization of the individual compounds was accomplished by NMR spectroscopy[11] and mass spectrometry.[12] Rigorous structural assignments for isomers **1a** and **1b** were achieved by reduction to the 6-methylbicyclo[3.2.0]heptanes, **3a** and **3b**, respectively, which were independently prepared from the *exo* and *endo* isomers of 7-methylbicyclo[3.2.0]hept-2-ene[1] by catalytic hydrogenation.

Thermal rearrangements were performed at 275°C in a gas-phase static reactor[13] and were monitored by analytical GC on an HP crosslinked 5% phenyl methyl silicone column (25 m×0.2 mm×0.33 μm film thickness). Whereas **1a** did not decay relative to the internal standard cyclooctane, the first-order rate constant for **1b** was found to be 7.3 (±0.4)×10^{-6} s^{-1} (correlation coefficient = 0.998), a value comparable to that reported for bicyclo[3.2.0]hept-2-ene at the same temperature.[1] The only isomer observed in the thermal reaction mixture derived from **1b** was *exo*-5-methylnorbornene, which reached a maximum concentration of approximately 2%. Significantly, no **1a** was observed in any product mixture over 27 hours, corresponding to one half-life for **1b**. Because **1a** is stable under the reaction conditions, this observation precludes a kinetically competitive ring inversion process involving the 6-methylbicyclo[3.2.0]hept-2-enes at this temperature.

This study also has implications for the interconversion of *exo*- and *endo*-7-methylbicyclo[3.2.0]hept-2-enes. The C_1–C_5 cleavage and ring inversion path (Scheme 1) should be more competitive for the 6-methyl pair of isomers than for their 7-methyl counterparts, since C_1–C_7 cleavage would yield a primary radical center at C_7 for the diradicals derived from **1a** and **1b**. That *endo–exo* equilibration is not observed for the 6-methyl epimers provides a strong indication that no ring inversion process is involved in the interconversion of the 7-methylbicyclo[3.2.0]hept-2-enes. This is an important discovery because the potential for C_7 epimerization has not routinely been considered in other thermal studies of the bicyclo[3.2.0]hept-2-ene system.

A definitive experimental confirmation of this implication may be secured through a stereochemical test: our current mechanistic hypothesis (C_7 epimerization, not ring inversion) predicts that (1*S*,5*S*,7*S*)-7-methylbicyclo[3.2.0]hept-2-ene (**4b** in Scheme 1) would isomerize thermally to (1*S*,5*S*,7*R*)-7-methylbicyclo[3.2.0]hept-2-ene (**4a**), not to the (1*R*,5*R*,7*S*) isomer **4a**′. Experimental tests with chiral substrates are in order.

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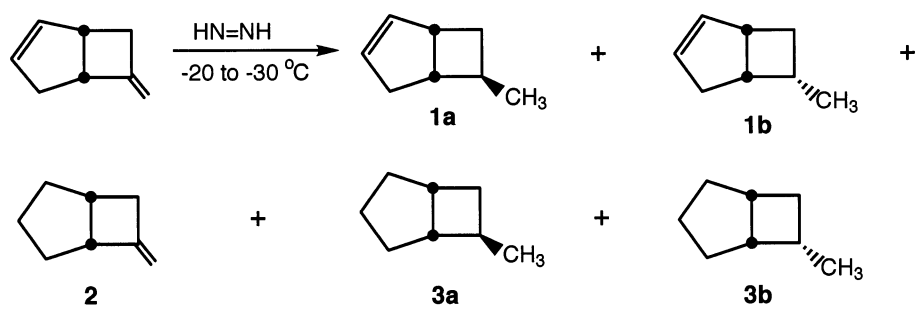

Scheme 2. Product mixture from low-temperature diimide reduction of 6-methylenebicyclo[3.2.0]hept-2-ene.

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10. Preparative GC elution order was as follows: **3a** (7.2 min), **1a** (8.7 min), **3b** (9.8 min), **1b** contaminated with **2** (12.8 min), and unreacted 6-methylenebicyclo[3.2.0]hept-2-ene (21.3 min). The component **2** in **1b** proved useful as an internal standard[14] for GC analyses of reaction mixtures. On the analytical GC column, **2** had a retention time of 4.6 min; **1b**, 4.7 min.
11. ^{13}C NMR ($CDCl_3$, ppm): **1a**, 134.7, 130.3, 44.1, 41.9, 39.9, 35.8, 35.1, 21.6 (CH_3); **1b**, 135.7, 131.7, 43.3, 37.5, 34.9, 33.6, 29.2, 17.4 (CH_3); **3a**, 46.0, 33.5, 33.1, 32.9, 32.3 (two overlapping peaks), 25.1, 22.8 (CH_3); **3b**, 40.9, 35.5, 32.6 (two overlapping peaks), 27.4, 26.7, 26.4, 15.4 (CH_3). The ^1H NMR spectra for **1a**, **1b**, **3a**, and **3b** at 300 MHz are not first-order; the methyl doublets, however, are readily discernible: **1a**, δ 1.1; **1b**, δ 1.0; **3a**, δ 1.1; **3b**, δ 0.8. The shielding of the *endo*-methyl is apparent in both the ^1H and ^{13}C NMR spectra.
12. Mass spectral data were acquired on all compounds in the diimide reduction mixture: **1a**, 108 (2.5%), 66 (100%); **1b**, 108 (2%), 66 (100%); **3a**, 110 (2%), 68 (100%); **3b**, 110 (2%), 68 (100%); 6-methylenebicyclo[3.2.0]hept-2-ene, 106 (3%), 91 (100%), 66 (84%); **2**, 108 (14%), 93 (100%), 79 (85%).
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