

Stereochemistry of the Thermal Retro-Diels–Alder Reactions of *cis,exo*-5,6-*d*₂-Bicyclo[2.2.1]hept-2-ene, *cis*-4,5-*d*₂-Cyclohexene, and *cis,exo*-5,6-*d*₂-Bicyclo[2.2.2]oct-2-ene

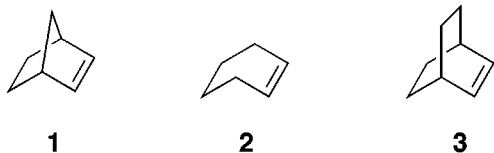
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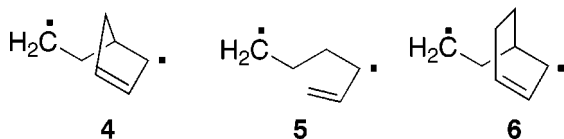
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Recent femtosecond dynamics experiments and theoretical studies on retro-Diels–Alder fragmentations of bicyclo[2.2.1]hept-2-ene (**1**), cyclohexene (**2**), and bicyclo[2.2.2]oct-2-ene (**3**) have addressed fundamental mechanistic and conceptual issues.^{1–4} Are two carbon–carbon single bonds broken simultaneously or sequentially? What evidence might respond to this question? What factors determine the relative importance of concerted versus stepwise reaction channels? Are the concepts associated with “concert”, “concerted”, and “concertedness” fully understood?



Under the gas-phase pump–probe reaction conditions of femtosecond-resolved dynamic studies, **1**, **2**, and **3** give transients characterized by low ionization energies, masses equal to those of the starting materials (94, 82, and 108 amu), and decay times of about 200 fs. These species are thought to be the diradicals **4**, **5**, and **6**; stepwise processes as well as concerted fragmentations appear to be involved.^{1,2} Under the high-energy photochemical reaction conditions, rapid conversions of ¹($\pi\pi^*$) to ground-state surfaces may lead directly to diradicals not easily accessible through thermal experiments, which begs the question: Are these diradicals accessible thermally?

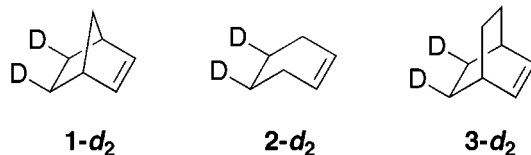


From gas-phase ΔH_f data for **1**,^{5,6} **2**,⁷ and **3**,^{8,9} and from experimental ΔH^\ddagger data for the retro-Diels–Alder reactions shown

by **1**,^{10,11} **2**,^{12,13} and **3**,^{8,14} one may derive ΔH_f estimates for the respective transition structures leading to fragmentations. Theory-based estimations of ΔH_f for the corresponding diradicals **4**, **5**, and **6** show that the transition structures of the “concerted” retro-Diels–Alder reactions are of lower energy than the alternative diradical structures: the difference between them, the “transition state resonance energy”, is invariably negative.¹⁵

These energy gaps between the alternatives available to **1**, **2**, and **3** have been estimated by using force-field MM2ERW calculations for the diradicals **4**, **5**, and **6**: –13.7, –5.7, and –5.1 kcal/mol, respectively.^{15,16} The same comparisons derived from calculations at the B3LYP/6-31G(d) level of theory lead to a similar but more compressed sequence of energy differences: –7.4, –4.1, and –1.1 kcal/mol.² The difference is large for **1**, modest for **2**, and small (maybe too close to call) for **3**. Thus, were these energy differences the dominant consideration, retro-Diels–Alder substrate **1** should be *least* likely to react by way of a diradical intermediate, and bicyclooctene **3** should be *most* likely to have diradical mediated reaction channels in serious competition with a concerted fragmentation.

Gas-phase static-reactor studies have shown that norbornene (**1**) fragments in a stereochemically conservative fashion: *cis,exo*-5,6-*d*₂-bicyclo[2.2.1]hept-2-ene (**1-d**₂) gives (*Z*)-*d*₂-ethylene.^{17,18} Cyclohexene **2-d**₂, however, when heated in a shock tube at 821 or 907 °C, gives rise to both isomers of *1,2-d*₂-ethylene, evidence implicating diradical and vinylcyclobutane intermediates.^{19,20}



From this experimental evidence on the stereochemistry of retro-Diels–Alder reactions of **1-d**₂ and **2-d**₂ and the thermochemical trends noted above one might anticipate that **3-d**₂ would fragment with an even greater loss of stereochemistry, indicative of a more dominant role played by a diradical intermediate. This anticipation has now been tested experimentally.

Retro-Diels–Alder fragmentations at temperatures of 526–744 °C and at total gas pressures under reaction conditions exceeding 2 atm of 2.00% **1**, 2.00% **1-d**₂, 1.93% **3**, or 1.96%

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3-d₂ in argon were conducted with a 2.54 cm i.d. single-pulse shock tube;²¹ the reaction temperatures were calculated from the extent of decomposition of the reactant and the previously established Arrhenius parameters for decomposition of **1**, $\log(A, \text{s}^{-1}) = 14.63$ and $E_a = 45.39$ kcal/mol,²² and of **3**, $\log(A, \text{s}^{-1}) = 15.12$ and $E_a = 57.3$ kcal/mol.⁸ Under these reaction conditions, both reactions may be treated as irreversible first-order reactions at the high-pressure limit.

The stereochemical characteristics of the 1,2-d₂-ethylenes formed were determined by tunable diode laser (TDL) infrared absorption spectroscopy,^{19,23,24} a precise and accurate technique appropriate for examining the very small ethylene samples produced through the shock tube conversions free from surface-catalyzed processes. It provides a huge ($\sim 10^{-5}$ wavenumber) resolution and zero-baseline separation of rotation–vibration absorption features characteristic of individual components in mixtures of (*Z*)- and (*E*)-d₂-ethylenes in the presence of other deuterium-labeled ethylenes and CH₂=CH₂.

Authentic samples of ethylene, *d*-ethylene, (*Z*)-d₂-ethylene, (*E*)-d₂-ethylene, and 1,1-d₂-ethylene were scanned over the range 1025–1035 cm⁻¹ to identify a small wavenumber range (typically 0.1 cm⁻¹) at which all species of interest have strong but nonoverlapping absorption features and to determine the intensities of those features. Then ethylene products from the shock tube runs were isolated by distillation from a pentane slush bath and analyzed over the same spectral region. Each recorded TDL spectrum consisted of 50 overlaid scans collected over 1 s, an optimal scan time for maximizing the signal-to-noise ratio while minimizing drift-induced broadening of absorption features.

From a sample of **1-d₂**, heated to 576 °C, (*Z*)-d₂-ethylene was observed but no (*E*)-d₂-ethylene was detected, a finding anticipated from the thermochemical situation and earlier work.^{17,18} From a sample of **3-d₂**²⁵ heated to 744 °C, the product ethylene sample contained unlabeled ethylene and (*Z*)-d₂-ethylene, as expected, but no absorption bands characteristic of (*E*)-d₂-ethylene were detected, an outcome not at all consistent with the thermochemical-based trends outlined above and the presumption that they would correlate with the relative importance of concerted versus stepwise paths and with reaction stereochemistry.

Cautious interpretation of the TDL data requires less absolute conclusions on reaction stereochemistry. How much (*E*)-d₂-ethylene could have been present and yet undetected in product mixtures from **1-d₂** or **3-d₂**? To establish the definite presence of (*E*)-d₂-ethylene would require an absorbance value of 0.005 for a feature characteristic of this ethylene, twice the noise level in a recorded spectrum. This would correspond to an (*E*)-d₂-ethylene pressure in the spectrometer cell of 0.010 Torr. In comparison, the observed intensity of the (*Z*)-d₂-ethylene features in the product sample from **1-d₂** corresponds to a sample pressure of 0.74 Torr, establishing a **minimum** *Z*:*E* ratio of 74:1. Thus, (*E*)-d₂-ethylene could not have exceeded 1.3% of the d₂-ethylene produced from **1-d₂** at 576 °C. Performing the same analysis on the absorption data from the **3-d₂** product produced a **minimum** *Z*:*E* ratio of 16:1, or a maximum (*E*) isomer percentage of 6.3% of the 1,2-d₂-ethylene produced at 744 °C.

The less definitive (*Z*)/(*E*) ratio in the d₂-ethylenes from **3-d₂** is due to the smaller measured amount of (*Z*) isomer in the sample, 0.16 Torr. This results from three experimental limitations. First,

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(25) The sample of **3-d₂** was prepared from *endo*-bicyclo[2.2.2]oct-5-ene-2,3-dicarboxylic anhydride (Aldrich) through reduction with deuterium, hydrolysis to the d₂-diacid, and oxidative bisdecarboxylation with Cu₂O, 2,2'-dipyridyl, powdered glass, and quinoline at 140–185 °C (compare: Snow, R. A.; Degenhardt, C. R.; Paquette, L. A. *Tetrahedron Lett.* **1976**, 4447–4450). It was of >99% purity, by capillary GC.

the process of heating a larger molecule (larger heat capacity) to a higher temperature necessitated starting with a smaller reactant sample pressure in the shock tube. Second, the experiment with **3-d₂** converted only 25% of the reactant to products, whereas the **1-d₂** experiment achieved 32% conversion. Third, and most important, **3-d₂** can undergo retro-Diels–Alder decomposition in either of two ways, to give CH₂=CH₂ or CHD=CHD; <6.3% of CHD=CHD isomers is equivalent to <3.2% of all ethylenes in the product mixture. These limitations notwithstanding, the maximum amount of undetected (*E*)-d₂-ethylene from **3-d₂** could not have been comparable to, let alone greater than, that produced and easily seen and quantified in the earlier experiments on **2-d₂**, 5–6% at 821 °C and 8–9% at 907 °C, involving smaller extents of retro-Diels–Alder reaction.

The stereochemical aspects of the retro-Diels–Alder reactions of **1-d₂**, **2-d₂**, and **3-d₂** do not follow the thermochemical trends. The bicyclic hydrocarbons **1-d₂** and **3-d₂** give only (*Z*)-d₂-ethylene, to within current detection limits, while **2-d₂** fragments to give both the (*Z*)-isomer and an easily seen and quantified fraction of the (*E*)-isomer.¹⁹

Geometrical constraints may account for these striking differences in reaction stereochemistry. Were one of the two C–C bonds to be broken in **3-d₂** to become longer, the other would become weaker, for the second bond would be kept well aligned for interaction with both the developing allylic π-system and the adjacent C1–C6 bond. Unless selective elongation of C1–C6 were to proceed so substantially that rotation about C5–C6 could complete the act of bond breaking and simultaneously increase the strength of the C4–C5 bond, the stereochemical outcome could be conservative, even though the two bond cleavages were highly asynchronous or stepwise. In **2-d₂**, however, vibrationally excited molecules have access to conformations in which one C–C bond can break while the second destined to cleave is approximately coplanar with the allylic carbons, thus permitting formation of the diradical and further reaction to give butadiene and ethylene in a stereochemically nonconservative fashion.

Dynamics and timing issues sensitive to geometrical constraints versus conformational freedoms rather than only orbital symmetry factors or thermochemical considerations could be responsible for overall reaction stereochemistry. The greater overall stability of **2** vs **3** and the considerably higher temperature needed to induce retro-Diels–Alder decomposition of **2** may also contribute to the difference in reaction stereochemistry. At higher temperatures, more of the vibrations of **2** are highly excited, possibly leading to more rapid loss of stereochemistry in diradical intermediate **5**.

Whatever the full explanation, it seems likely that thermal Diels–Alder and retro-Diels–Alder reactions involve families of trajectories over the transition region of the potential energy surface, permitting nonconcerted, stereochemically nonconservative processes, as in the cyclohexene to butadiene plus ethylene fragmentation,^{19,20} whenever geometrical constraints do not impose preemptive limits on conformational options. Conformational opportunities and entropic factors, not only orbital symmetry and enthalpic considerations, may well control reaction stereochemistry.²⁶

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