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Effect on Kinetics by Deuterium in the 1,5-Hydrogen Shift of a Cisoid-Locked 1,3(*Z*)-Pentadiene, 2-Methyl-10-methylenebicyclo[4.4.0]dec-1-ene: Evidence for Tunneling?

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Abstract: Prompted by extensive theoretical interest in the role of tunneling in the intramolecular 1,5-hydrogen shift in 1,3(*Z*)-pentadienes and the large uncertainty in the published values of the theoretically relevant kinetic deuterium-isotope effect and its dependence on temperature, we have examined a degenerate bicyclic version, 2-methyl-10-methylenebicyclo[4.4.0]dec-1-ene, which is locked into the rearrangement-competent cisoid conformation, in the hope of obtaining more precise and accurate values. From rate constants determined over a range of 33 °C from 167.7 to 201.6 °C, Arrhenius parameters, $E_a = 32.8 \pm 0.4$ kcal mol^{-1} and $\log A = 11.1 \pm 0.2$, were obtained. An average kinetic isotope effect of 4.2 ± 0.5 obtained from all values for k_H/k_D and k_{-H}/k_{-D} may be compared with a value of 5.0 ± 0.3, recalculated from data in the pioneering publication of Roth and König. From a highly problematic extrapolation of the temperature dependence, a value of k_H/k_D of 16.6 (standard error between 6.5 and 43) is calculated for the kinetic isotope effect at 25 °C (Roth and König: 12.2). With curvature in Arrhenius plots being one of the three types of experimental evidence considered indicative of tunneling, the kinetic study of the previously published rearrangement of 1-phenyl-5-*p*-tolyl-1,3(Z)-pentadiene has been extended over a period of 339 days to a range of 108 °C (77−185 °C) without discerning any deviation from a straight-line Arrhenius plot: $E_a = 28.7 \pm 0.5$ (kcal mol^{-1}) and $\log A = 9.41 \pm 0.30$.

Introduction

Several theoreticians have shown interest for a third of a century in the strongly concerted, thermally activated 1,5-hydrogen shift undergone by 1,3(*Z*)-penta-1,3-diene as a reaction in which tunneling may play a significant role.[1−6] The attractiveness of this example has stemmed not merely from the high value of 5.3, reported by Roth and König for its deuterium kinetic isotope effect (KDIE), but more from its extrapolation to a value of 12.2 at room temperature by means of the ratio of the Arrhenius equations for k_H and k_D (Figure 1).[7a] The elegant elucidation of the stereochemistry of the reaction, also by Roth and König,[8] in full confirmation of the original proposal by Wolinsky and co-workers[9a] (later given theoretical support by Woodward and Hoffmann) has contributed in no small measure to the attractiveness of this reaction for theoretical exploration.[9b]

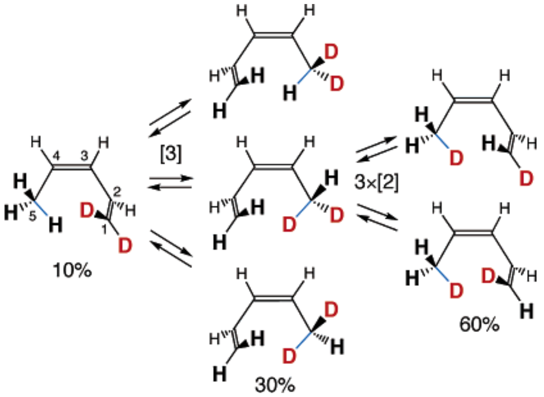

Figure 1. Thermal rearrangement of 1,1-dideuterio-1,3(*Z*)-pentadiene is depicted, as are the relative, statistically determined concentrations expected at equilibrium in the *absence* of secondary deuterium isotope effects.

Critical to the evaluation of the quantitative predictions from theoretical investigations is the availability of reliable experimental observations for direct comparison. The only report in

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Table 1. Specific Rate Constants and Derived Arrhenius Parameters (including Recalculations) Reported in Roth and König[7] for the Disappearance of 1,1-Dideuterio-1,3(Z)-pentadiene (k_H) and 5,5,5-Trideuterio-1,3(Z)-pentadiene (k_D)

T °C	185.0	190.1	190.2	195.1	200.0	205.3	210.6
k_H[a]	1.38		1.80	3.13	4.47	7.10	
k_D[a]		0.394		0.600	0.90	1.38	2.26
k_H/k_D			4.57	5.22	4.97	5.14	
R/K	$k_H = 2.8 \times 10^{11} \exp(-36\,300 \pm 500)^b/RT\ \text{sec}^{-1}$						
recalcd[c]	$k_H = 2.19 \times 10^{11} \exp(-36\,100 \pm 2\,160)/RT\ \text{sec}^{-1}$ ($\log A = 11.34 \pm 1.00$)						
R/K	$k_D = 2.4 \times 10^{11} \exp(-37\,700 \pm 500)/RT\ \text{sec}^{-1}$						
recalcd[c]	$k_D = 2.36 \times 10^{11} \exp(-37\,670 \pm 680)/RT\ \text{sec}^{-1}$ ($\log A = 11.37 \pm 0.31$)						

[a] In units of 10^{-6} sec^{-1}; no estimates of experimental uncertainties given,[7a] nor are any available in König's dissertation.[7b] [b] ±1300 cal mol^{-1} in König's dissertation. [c] Uncertainties are standard errors as provided by the Anova regression analysis in Microsoft Excel.

the literature on the paradigm, 1,3(Z)-pentadiene, comes from the investigation of Roth and König. Although their ratios of k_H to k_D (KDIE) in the temperature range, 190.2−205.3 °C, 5.0 ± 0.3, seem quite reliable, as noted in a recent examination of the effect of radical-stabilizing phenyl substituents on the 1,5-hydrogen shift,[10] their specific rate constants and derived Arrhenius parameters for the KDIE are of insufficient precision for extrapolation to room temperature to serve as a reliable basis for comparison with theory.[11] This inadequacy is fully to be understood in light of having only 60 MHz NMR at their disposal and, consequently, being limited to a study of the disappearance of their educts, 1,1-dideuterio-1,3(Z)-pentadiene and 5,5,5-trideuterio-1,3(Z)-pentadiene, rather than a full study as outlined in Figure 1. From the tabulation of their data and calculations in Table 1, the limitations are clear.

As reported by Roth and König, temperature dependence of k_H/k_D can be estimated from the ratio of the Arrhenius expressions in Table 1 (rows five and seven), whence $\ln(k_H/k_D) = 0.154 + (1400 \pm 700)/RT$ [$(k_H/k_D)_{25°C} = 12.4$ (3.8 to 41); $A_H/A_D = 1.17$], or from the recalculated kinetic results given in rows six and eight: $\ln(k_H/k_D) = -0.14 \pm 1.60 + (1570 \pm 2400)/RT$ [$(k_H/k_D)_{25°C} = 12.3$; $A_H/A_D = 0.94$]. Calculation directly from the ratios of k_H/k_D at the four temperatures collected in the fourth row of Table 1 affords $\ln(k_H/k_D) = (4.45 \pm 2.28) + (-1340 \pm 1070)/RT$. Here, also, the uncertainties in the calculated value for k_H/k_D are too large for a credible extrapolation to room temperature: $k_H/k_D = 8.9$ (1.5−54 in neglect of any uncertainty in the constant, $\ln(A_H/A_D) = 4.45$).

Stimulus for the present paper stems less from a desire to confirm the experimental values for the ratios of k_H/k_D at the higher temperatures than from a hope to provide a more reliable basis for extrapolation of the ratio to room temperature. For this study, deuterated 2-methyl-10-methylenebicyclo[4.4.0]dec-1-ene (**1** and **1′** of Figure 2) has been chosen. By its bicyclic constitution, it is the first 1,3(Z)-pentadiene to be fully locked into the cisoid conformation essential for the realization of the 1,5-hydrogen shift and, therefore, freed of any need to consider the complicating factor introduced by the rearrangement-incompetent, usually thermochemically more stable transoid conformation of the acyclic paradigm.[12]

Given the vastly increased analytical power of currently available NMR spectroscopy, we have aspired to elucidate the interconversions among all three isotopomers. Each has a different statistical factor that sets a theoretical ratio of 1:3:6 at equilibrium (in explicit neglect of secondary isotopic perturbations on the position of equilibrium). These factors stem from the three possible ways of arranging the atoms in both the monodeuterio- and dideuteriomethyl groups and the two arrangements possible in the monodeuteriomethylene group (Figure 1).

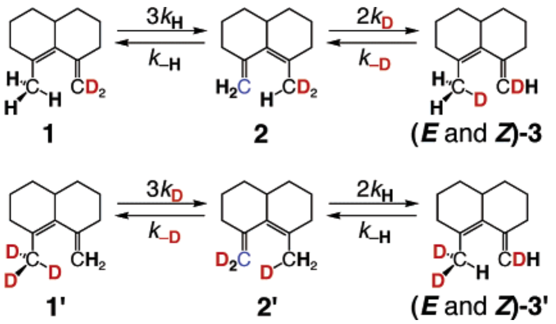
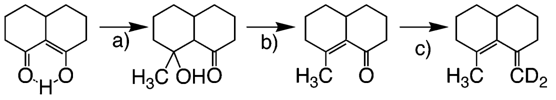


Figure 2. Interconversion by thermal 1,5-hydrogen shift is shown in the two sets of the three isotopomers of 2-methyl-10-methylenebicyclo[4.4.0]-dec-1-ene deuterium-labeled, respectively, in the methylene group and the methyl group.

Scheme 1



a) CH_3MgI/ether b) *p*-toluene sulfonic acid
c) di(trideuteriomethyl)titanocene

Preparation

Preparation was accomplished by the unexceptional sequence shown in Scheme 1, starting from bicyclo[4.4.0]decan-2,10-dione (fully enolized). Methylation of the diketone, although presumably a reaction of its anion, proceeded satisfactorily with methylmagnesium iodide. But note how weakly acidic the enolizable diketones fixed in the cis configuration are.[13] For the conversion of 2-methylbicyclo[4.4.0]dec-1-en-10-one to 2-methyl-10-methylenebicyclo[4.4.0]-dec-1-ene, the procedure pioneered by Petasis that employs dimethyl titanocene offered a substantial improvement over the classical Wittig procedure.[14] (We did not explore an improved method introduced by Hasselmann.)[15] The deuterium analogues, **1** and **1′** of Figure 2, were prepared by the same sequences by employing trideuteriomethyl reagents.

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(11) Although Chantranupong and Wildman, for example, have noted explicitly that "...the error in the slope (of ln k_H/k_D) is about 50% according to Roth and König (1.4 ± 0.7 kcal mol^{-1})," they have little alternative but to conclude that a "frequency of 390 cm^{-1} provides reasonable agreement with experiment."[5] Liu et al. have concluded that "tunneling can indeed account for the strong temperature dependence observed experimentally as well as for the magnitude of the KIEs."[6]

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Table 2. Specific Rate Constants for the 1,5-Hydrogen Shift in 2-Methyl-10-dideuteriomethylenebicyclo[4.4.0]dec-1-ene (**1**) and 2-Methylene-10-trideuteriomethylbicyclo[4.4.0]dec-1-ene (**1′**)

2-Methyl-10-dideuteriomethylenebicyclo[4.4.0]dec-1-ene (**1**)

$3k_H$[a,b]	k_{-H}	$2k_D$	k_{-D}
	201.6 ± 0.2 °C		
9.73 ± 0.16 (1.61)[c,d]	*3.29* ± 0.13 (3.80)	*1.73* ± 0.043 (2.46)	*1.00* ± 0.038 (3.75)
10.01 ± 0.10 (0.98)[c,d]	3.43 ± 0.078 (2.28)	1.66 ± 0.024 (1.44)	0.90 ± 0.020 (2.25)
	184.4 ± 0.25 °C		
2.70 ± 0.032 (1.20)[c,d]	*0.911* ± 0.028 (3.09)	*0.425* ± 0.010 (2.23)	*0.249* ± 0.009 (3.63)
2.65 ± 0.034 (1.29)[c,d]	0.925 ± 0.026 (2.85)	0.419 ± 0.011 (2.57)	0.226 ± 0.010 (4.33)
	167.9 ± 0.2 °C		
0.691 ± 0.008(1.11)[c,d]	*0.245* ± 0.006 (2.42)	*0.104* ± 0.002 (1.71)	*0.060* ± 0.0016 (2.74)
0.697 ± 0.009(1.31)[c,d]	0.251 ± 0.007 (2.79)	0.090 ± 0.002 (1.96)	0.0494 ± 0.0017(3.37)

2-Methylene-10-trideuteriomethylbicyclo[4.4.0]dec-1-ene (**1′**)

$3k_D$	k_{-D}	$2k_H$	k_{-H}
	167.7 ± 0.2 °C		
0.135 ± 0.0011(0.8)[d,e]	*0.0461* ± 0.0015 (3.2)	*0.430* ± 0.012 (2.9)	*0.202* ± 0.0067 (3.3)
0.131 ± 0.0023(1.7)[d,f]	0.0433 ± 0.0030(6.9)	0.386 ± 0.022(5.8)	0.185 ± 0.013 (6.8)

[a] For the definition of the specific rate constants, see Figure 2. [b] Specific rate constants, in units of 10^{-5} sec^{-1}, are calculated from the corrected data given in Table SI-5. [c] Values in italics are based on NMR measurements of the methyl groups: CH_3 1.81, CH_2D 1.78, CHD_2 1.76 ppm (δ) (method *a*); those in plain type are based on the methyl group: CH_3 1.81, the $=CH_2$ group 5.01 and 4.78, and the $=CHD$ group 5.00 and 4.76 ppm (δ) (method *b*). [d] Values in parentheses are uncertainties at the 95% confidence level in %. [e] Analytical results for **1′** are based on ^1H NMR signals (method *c*) in Table SI-4 as corrected in Table SI-5. [f] Analytical results by method *d* (Tables SI-4 and SI-5)).

Kinetics

Rates of the disappearance of **1** and the appearance of **2** and (*E* and *Z*)-3 are followed by ^1H NMR analysis on a 600-MHz instrument, but even at this strong field, the resolving capacities are stretched to the limit. Two sets of results in Tables SI-1, SI-2, and SI-3 of the Supporting Information relating changes in concentration with time at three temperatures are based on the signals given in Table 2, footnote *c*. In both methods of analyses, baseline separation is nearly, but not completely, achieved. We favor method *a* because quantitative evaluation by the second method *b* of the relative intensity of the two stereoisomeric hydrogen atoms in the methylene group falls short of equality by 10%, despite extensive variation of the relevant operating parameters of the NMR apparatus and the use of the 500-MHz instrument as well. This arcane phenomenon persists in three other examples, which will be discussed at greater length in the future.[16] The possibility that the phenomenon is related to the use of NMR tubes made of borosilicate glass has been explored by substituting soft glass tubes. The small differences in concentrations at 201.6 °C for reaction times of 112 and 205 h are not significant within experimental uncertainties (Table SI-6 in Supporting Information).

Specific rate constants are calculated by numerical integration by the program KINETIK of Dr. R. Fink.[17] This program employs a Runge−Kutta procedure of fourth order, allows up to seven components to be handled by ad libitum kinetic schemes, and incorporates the estimation of errors for the individual rate constants at the 95% confidence level by the method of Marquardt.[18] Results from methods *a* and *b* of analysis are collected in Table 2. Although the precision of the four calculated specific rate constants is about as good as it gets with NMR (2−4% at the 95% confidence level), the failure of the two sets of values to fully overlap within acceptable uncertainties points to a lower accuracy.

A further worry concerns the possibility that side products initiated by a second-order, ethene−ethene union to a 1,8-octa-2,6-diene diyl diradical may be corrupting analyses at the longer times of reaction. The activation energy of that type of *bimolecular* reaction is estimated to be ~24 kcal mol^{-1},[19] which is substantially lower than the activation energy of 36.3 kcal mol^{-1} reported for the *unimolecular* 1,5-hydrogen shift.[7]

Toward the end of each kinetic series, when no further significant change in relative concentrations was to be seen, the theoretical, symmetry-based values of 0.100, 0.300, and 0.600 had not been reached—a possible warning of a compromised accuracy or the impact of nontrivial secondary isotope effects. At 201.6 °C, values of approach to equilibrium were *0.107*, *0.326*, *0.567*, and 0.112, 0.312, 0.578; at 184.4 °C, *0.109*, *0.331*, *0.560*, and 0.115, 0.310, 0.579; at 167.9 °C, *0.108*, *0.328*, *0.564*, 0.114, 0.314, 0.572 (Tables SI-1, SI-2, and SI-3), and from **1′**, *0.109*, *0.285*, *0.606*, 0.112, 0.293, 0.595 (Table SI-4). On average, these values differ from the statistical by +11, +3.5, and −4%, respectively. A presentation in terms of specific rate constants is given in columns 2 and 3 of Table 3. These shortfalls weigh on the determination of k_H/k_D adversely.

From the resulting specific rate constants collected in Table 2, values for the ratios of k_H/k_D starting with **1** may be obtained from the values for $3k_H/2k_D$ (italics; propagation of errors): *3.75* ± 0.11 at 201.6 °C, *4.24* ± 0.11 at 184.4 °C, and *4.44* ± 0.09 at 167.9 °C, and from **1′**, *4.78* ± 0.14 at 167.7 °C (Table 3). These values are uniformly larger than those obtained from $k_{-H}k_{-D}$: *3.28*, *3.66*, *4.10*, and *4.38*, respectively.

Discussion

The rearrangement of **1** is not exceptional in being degenerate and requiring either racemization or isotopic labeling for its observation, but it is unique to our knowledge in being locked

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(16) This vexing aspect of the quantitative study of the kinetics of the 1,5-hydrogen shift will be addressed in greater detail in a forthcoming paper by Doering and Keliher.

(17) Roth, W. R.; Fink, R. Unpublished.

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Table 3. Degree of Approach to the Statistical Equilibrium, and Values of KDIEs (k_H/k_D) for the 1,5-Hydrogen Shift in 2-Methyl-10-dideuteriomethylenebicyclo[4.4.0]dec-1-ene (**1**) and 2-Methylene-10-trideuteriomethylbicyclo[4.4.0]dec-1-ene (**1′**) (Figure 2)

2-Methyl-10-dideuteriomethylenebicyclo[4.4.0]dec-1-ene (**1**)[a]

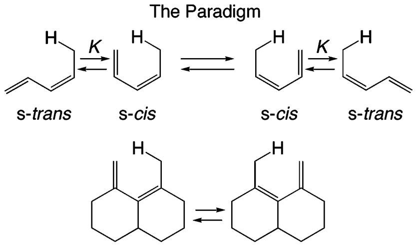
T, °C	approach to equilibrium		kinetic deuterium isotope effects[a]		
	$3k_H/k_{-H}$	$2k_D/k_{-D}$	$(2/3)(3k_H/2k_D)$	k_{-H}/k_{-D}	$(1/3)(3k_H/k_{-D})$
201.6	2.96	1.73	*3.75* ± 0.11	*3.28* ± 0.18	*3.24 ± 0.13*
201.6	2.94	1.84	4.05 ± 0.07	3.80 ± 0.12	3.71 ± 0.09
184.4	2.97	1.71	*4.24* ± 0.11	*3.66* ± 0.17	*3.61 ± 0.14*
184.4	2.87	1.86	4.22 ± 0.12	4.09 ± 0.21	3.91 ± 0.18
167.9	2.82	1.73	*4.44* ± 0.09	*4.10* ± 0.15	*3.84 ± 0.11*
167.9	2.78	1.83	5.16 ± 0.16	5.09 ± 0.22	4.70 ± 0.17

2-methylene-10-trideuteriomethylbicyclo[4.4.0]dec-1-ene **(1′)**

T, °C	approach to equilibrium		kinetic deuterium isotope effects[a]	
	$3k_D/k_{-D}$	$2k_H/k_{-H}$	$(3/2)(2k_H/3k_D)$	k_{-H}/k_{-D}
167.7	2.93	2.13	*4.78* ± 0.14	*4.38* ± 0.20
167.7	3.03	2.09	4.42 ± 0.27	4.27 ± 0.42

[a] Based on the specific rate constants given in Table 2 (data in italics and plain type have the same significance as in footnote *c* of Table 2). [b] Propagation of errors in the specific rate constants of Table 2.

Scheme 2



into the cisoid conformation indispensable to the occurrence of the intramolecular 1,5-hydrogen shift in 1,3(*Z*)-pentadienes (see Scheme 2). Although compound **1** is perturbed in other ways as well[20]—a certain rigidity imposed by its octalin configuration; by being tri-alkyl substituted at the 2, 3, and 4 positions—it nevertheless offers the opportunity of a comparison of enthalpy of activation with that of the paradigm, without *including* the equilibrium constant governing s-trans and s-cis (*K* in Scheme 2).

The Arrhenius parameters calculated from the rate constants for $3k_H$ listed in Table 2, which are the most precise, are $E_a = 32.8 \pm 0.4$ kcal mol^{-1} and $\log A = 11.1 \pm 0.2$. These parameters are the first defining the 1,5-hydrogen shift in a cisoid-locked 1,3(*Z*)-pentadiene. Comparison with the values given by Roth and König for the paradigm, $E_a = 36.3 \pm 0.5$ kcal mol^{-1} and $\log A = 11.45$, reveals a difference of 3.5 kcal mol^{-1} (in neglect of experimental uncertainties), which compares well with the difference of 3.7 kcal mol^{-1} in heat of formation of the transoid and cisoid conformations of 1,3(*Z*)-pentadiene calculated by Saettel and Wiest.[12]

Values of KDIE and their response to changes in temperature constitute one of the prominent manifestations of the tunneling effect. The KDIE of deuterium-perturbed compounds **1** and **1′** at the higher temperatures (201.6, 184.4, and 167.9 °C), where specific rate constants are conveniently accessible within comfortable lengths of times of measurement, are collected in Table 3 as values of k_H/k_D [$(2/3)(3k_H/2k_D)$] and k_{-H}/k_{-D}. They vary over a disappointingly large range of 3.28−5.16 but have average values of *4.14*, 4.48 (column 4), and *3.68*, 4.33 (column 5), and an overall average of 4.2 ± 0.5. Another estimate may be made by combining the data in Table 2 at 167.9 °C for $3k_H$ from **1** with that at 167.7 °C for $3k_D$ from **1′**. The resulting values of k_H/k_D, *5.12* ± 0.10 and 5.32 ± 0.12 (propagation of errors), are in good, possibly accidental, agreement with the value, 4.91 ± 0.36, derived from the combined values of k_H/k_D of Roth and König obtained over the temperature range, 190.1−205.3 °C (Table 1). (Kloosterziel and ter Borg report a value of 5.0 in their study of the interconversion of 1,3,6- and 1,3,5-cyclooctatriene at 120 °C and a secondary isotope effect of 1.02 ± 0.02.)[21] A value for k_H/k_D of ∼4.5 ± 0.5 appears trustworthy.

The closest our design comes to freedom from secondary isotope effects is in the ratio $(1/3)(3k_H/k_{-D})$ (see Figure 2). The resulting values are as widely spread as those derived from $(2/3)(3k_H/2k_D)$ (see Table 2).

Temperature dependence of the KDIE is one of three generally accepted, operational criteria bearing on a role for tunneling.[22] An unexpected increase in the KDIE at lower temperatures should become observable in a range of temperatures where the temperature-independent tunneling component is comparable to the temperature-dependent component of the overall rate.[23] Of the four sets of values at 201.6, 184.4, and 167.7 °C, two are from column 4 of Table 3, *3.75*, *4.24*, *4.44*, and 4.05, 4.24, 5.16, and two more are from column 5, *3.28*, *3.66*, *4.10*, and 3.80, 4.09, 5.09. Whether the increase at lower temperature in reality exceeds that expected from the higher enthalpy of activation of k_{Ds} is the question. That the precision of these data is insufficient to warrant extrapolation to room temperature emerges starkly from calculation of the temperature dependence of k_H/k_D from the eight values in Table 3 (column 4). The resulting Arrhenius equation, $\ln(k_H/k_D) = (-1.10 \pm 0.62) + (1170 \pm 280)/RT$ (standard errors at the 95% confidence level errors are ± 1.52 and ± 690 cal/mol, respectively), leads to a value extrapolated to room temperature of 16.8 (2−67!)

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(20) Not being up to a discussion with significant conclusions, we cite a model: Glass, D. S.; Boikess, R. S.; Dewar, M. J. S. *Tetrahedron Lett.* **1966**, *7*, 999−1008.

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(23) With tunneling, $(k_{obs})_H = A_H \exp(-E_a/RT) + (k_{tun})_H$. Because $(k_{tun})_D$ is expected to be very much smaller than $(k_{tun})_H$, $(k_{obs})_H/(k_{obs})_D = [A_H \exp(-(E_a)_H/RT) + (k_{tun})_H]/[A_D \exp(-(E_a)_D/RT)]$; only at temperatures where $A_H \exp(-(E_a)_H/RT)$ becomes comparable in magnitude to $(k_{tun})_H$ will $(k_{obs})_H/(k_{obs})_D$ begin to reflect tunneling.

for k_H/k_D at 25 °C.[24] Although this value falls in the same range as the value of 12.2 advanced by Roth and König for the paradigm and agrees with the value of 10.3 projected by Baldwin and Reddy for a related 1,7-hydrogen shift (note the drastically different geometry of the transition region),[22b] we believe the present effort has no more succeeded than that of Roth and König in providing experimental values of k_H/k_D of sufficiently high accuracy to serve theoreticians as a reliable check on their calculations of the low-temperature KDIE and the tunneling component in the 1,5-hydrogen shift. Along with Hayase, Hrovat and Borden in footnote 11 of their recent paper,[25] we note that the good agreements of the value of 36.6 calculated by Saettel and Wiest[12] and those of Jiao and Schleyer of 36.9 and 34.9 kcal mol^{-1} [26] with the experimental value of Roth and König[7] of 36.3 kcal mol^{-1} for s-*trans*-1,3(*Z*)-pentadiene were obtained in neglect of a tunneling component.

Curvature in the Arrhenius plot constitutes a third, closely related criterion advanced as a manifestation of tunneling.[27] Indeed Chantranupong and Wildman note, "Because the Arrhenius plots for hydrogen transfer show no indication of curvature, it might seem that this reaction can be described in terms of a conventional, thermally activated process."[5] This criterion has now been pursued more searchingly by adding to the published kinetic study of the kinetics of rearrangement of 1-*p*-tolyl-5-phenyl-1,3(*Z*)-pentadiene[10] an extension to lower temperatures over a necessarily much longer period of time. After 339 days (29 289 600 s), we can now report reliable specific rate constants of $3.58 \pm 0.20 \times 10^{-9}$ s^{-1} and $2.82 \pm 0.14 \times 10^{-8}$ s^{-1} at 77.1 °C and 98.4 °C, respectively (95% confidence level). When combined with the published rate constants at 153.7 and 185.2 °C,[10] these new data give a straight-line Arrhenius plot with no sign of curvature over the 108 °C range of temperature. The resulting Arrhenius equation has the parameters: $\ln k = (21.7 \pm 0.7 - (14{,}420 \pm 265)/T$; $E_a = 28.7 \pm 0.5$; and $\log A = 9.41 \pm 0.3$ ($\Delta H^{\ddagger}_{(404.3\mathrm{K})} = 27.9$). These values remain little changed from those reported earlier on the basis of rate constants at the two higher temperatures ($E_a = 30.1 \pm 0.9$ kcal mol^{-1} and $\log A = 10.14 \pm 0.9$). Attention is directed to a value for $\Delta H^{\ddagger}$ recently calculated by Hayase, Hrovat, and Borden for 1,5-diphenyl-1,3-(*Z*)-pentadiene of 32.6 kcal mol^{-1} (no estimate of uncertainty given). The discrepancy of 4.7 kcal mol^{-1} is probably not due to the presence of one *p*-methylphenyl group in place of the second phenyl.

At least over this 108 °C range of temperature, there is no indication of a curvature that might indicate a tunneling effect. Even though there is an experimentally verifiable contribution from tunneling, the temperature-dependent Arrhenius component of the rate is still too large at our lowest temperature relative to the rate of the putative, temperature-independent tunneling component to make an experimental observation of an increase in the KDIE possible.[27] In the investigations of Platz and coworkers, by contrast, hydrogen abstraction by diphenylcarbene at very low temperatures gives convincing evidence for tunneling.[28] For most organic chemists, the deliberate slowing of reactions by lowering temperatures seems without question a step in the wrong direction! None the less, we look forward to predictions from the calculational and theoretical community of a range of temperature within which the two components of the experimental rates of the 1,5-hydrogen shift become comparable and attention to the tunneling component is demanded. Above such ranges of temperature, the tunneling effect is likely, in the opinion of some, to remain relegated to the virtual world of calculation.

Experimental Section

General Procedures. NMR spectra, ^{1}H (400 MHz) and ^{13}C (100.6 MHz), were measured in $CDCl_3$ and, unless otherwise noted, on a Varian Mercury 400 instrument, whereas ^{1}H (500 MHz) and ^{13}C (125.7 MHz) spectra were measured on a Varian Unity/Inova 500 instrument. Chemical shifts are reported in ppm relative to tetramethylsilane (δ) with respect to residual C_6D_5H (7.15 ppm for ^{1}H and 128.0 ppm for ^{13}C). Spin−lattice relaxation times (T_1) were determined by the inversion−recovery method in benzene-d_6. Preparative GC on a Varian Aerograph A90-P3 instrument employed a 3-m column of 20% Carbowax 20M on Anachrom AS with He as a carrier gas. Analytical gas chromatography was conducted on a Hewlett-Packard (HP) 5890A gas chromatograph equipped with a J&W Scientific, Inc. DB-225 (cyanopropylphenyldimethylpolysiloxane) megabore column (0.53 mm i.d. × 30 m, 1 μm film thickness) and an HP 3393A integrator.

Bicyclo[4.4.0]decane-2,10-dione. A solution of ethyl 4-(3-oxocyclohexyl)-butyrate (1.2 g, 5.65 mmol, prepared according to the literature[29]) and sodium hydride (0.29 g, 12 mmol, 60% in mineral oil) in 15 mL of anhydrous benzene was boiled under reflux for 15 h. To the solution cooled in an ice bath, 20 mL of a 10% solution of KH_2PO_4 was added. Extraction twice with ether (30 mL each) gave an ether extract, which was washed with water, dried over anhydrous Na_2SO_4, filtered, concentrated, and subjected to column chromatography (silica gel, hexane/ethyl acetate, 20:1) to give 0.8 g (85% of theoretical yield) of the dione as pale-yellow crystals: ^{1}H NMR 0.84−0.89 (m, 1H), 1.14−1.25 (m, 3H), 1.61−1.71 (m, 2H), 1.82−1.93 (m, 3H), 2.34−2.46 (m, 4H), 16.17 (br s, 1H); ^{13}C NMR 21.67, 29.92, 33.96, 35.98, 110.76, 190.89.

2-Hydroxy-2-methylbicyclo[4.4.0]decan-10-one. To a solution of methylmagnesium iodide (prepared from 0.44 g of magnesium suspended in 15 mL of anhydrous ether under argon and 2.6 g of methyl iodide in 5 mL of anhydrous ether), 1.0 g (6 mmol) of bicyclo[4.4.0]-decane-2,10-dione in 6 mL of anhydrous ether was added slowly at 0 °C. After being stirred overnight at room temperature, the reaction mixture was quenched with saturated aqueous NH_4Cl, neutralized with 10% aqueous HCl, and extracted with 80 mL of ether. The ethereal extract was washed with water, dried over anhydrous Na_2SO_4, filtered, concentrated, and subjected to column chromatography (silica gel, hexane/ethyl acetate, 10:1 to 3:1) to give 0.57 g (52% of theoretical yield) of 2-hydroxy-2-methylbicyclo[4.4.0]decane-10-one as a pale-yellow oil: ^{1}H NMR (500 mHz, $CDCl_3$) 1.15−1.21 (m, 2H), 1.33−2.06 (m, 14H), 2.24−2.29 (m, 1H), 2.37−2.41 (m, 1H); ^{13}C NMR 22.35, 22.51, 24.80, 32.65, 34.56, 40.34, 40.71, 42.38, 63.80, 71.75, 214.24.

2-Methylbicyclo[4.4.0]dec-1-en-10-one. A solution of 0.57 g (3.1 mmol) of 2-hydroxy-2-methylbicyclo[4.4.0]decan-10-one in 30 mL of benzene containing 100 mg of *p*-toluenesulfonic acid in a 50-mL, round-bottomed flask fitted with a Dean−Stark trap was boiled under reflux

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(24) At room temperature (298.15 K) and in neglect of the uncertainties in ln *A*, $k_H/k_D = 16.6$ but ranges from 6.5 to 43 at the level of standard error and from 1.6 to 168 at the 95% confidence level!

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(26) Jiao, H.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1988**, *110*, 8223−8228.

(27) The Arrhenius plot of $\ln[(k_{obs})_H/(k_{obs})_D] = \ln(A_H/A_D) - [(E_a)_H - (E_a)_D]/RT$ is no longer linear when $(k_{tun})_H$ is added to the expression for $(k_{obs})_H$.

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(29) Knochel, P.; Berk, M. C. P. Y. S.; Talbert, J. *J. Org. Chem.* **1988**, *53*, 2392−2394.

for 2.5 h. The cooled reaction mixture was washed successively with saturated aqueous $NaHCO_3$, water, and brine to give a benzene solution, which was dried over anhydrous Na_2SO_4, filtered, concentrated, and subjected to column chromatography (silica gel, hexane/ethyl acetate, 10:1) to give 0.31 g (61% of theoretical yield) of 2-methylbicyclo-[4.4.0]dec-1-en-10-one as a colorless oil: ^{1}H NMR 1.18−1.24 (m, 1H), 1.31−1.44 (m, 2H), 1.61−1.70 (m, 2H), 1.80−1.96 (m, 6H), 2.05−2.08 (m, 2H), 2.22−2.30 (m, 2H), 2.43−2.48 (m, 1H); ^{13}C NMR 21.53, 21.99, 23.95, 31.01, 33.20, 33.98, 39.36, 43.19, 135.03, 143.57, 204.65.

2-Methyl-10-methylene-*d*$_2$-bicyclo[4.4.0]dec-1-ene (1). Trideuteriomethyllithium (22 mL of a 0.5 M solution in diethyl ether; 11 mmol) was added dropwise to a suspension of bis-cyclopentadiene titanium dichloride (1.25 g, 5 mmol) under argon at 0 °C. After 1 h, the mixture was quenched with cold D_2O and separated. The ethereal layer was dried over anhydrous Na_2SO_4, filtered, and concentrated to give orange crystals of bis-cyclopentadiene dimethyltitanium. This material was dissolved in 10 mL of anhydrous toluene and treated with the sample of 2-methylbicyclo[4.4.0]dec-1-en-10-one above in 5 mL of toluene. The reaction mixture was stirred at 75 °C in the dark for 46 h. The addition of hexane at room temperature precipitated solid material, which was removed by filtration. Concentration of the hexane phase and chromatography on basic alumina (hexane as eluant) afforded 0.17 g (54%) of 2-methyl-10-methylene-*d*$_2$-bicyclo[4.4.0]dec-1-ene as a pale-yellow oil: ^{1}H NMR (500 MHz, benzene-*d*$_6$) 1.07−1.14 (m, 2H), 1.38−1.46 (m, 2H), 1.56−1.60 (m, 1H), 1.64−1.71 (m, 3H), 1.80 (t, J = 0.98 Hz, 3H), 1.90−1.92 (m, 2H), 2.00−2.09 (m, 2H), 2.26−2.31 (m, 1H); ^{13}C NMR (125.7 MHz, benzene-*d*$_6$) 21.11, 22.08, 27.75, 31.94, 32.59, 35.58, 37.32, 39.85, 127.28, 135.70, 148.06; exact mass HRMS (EI) calcd for $C_{12}H_{16}D_2$ 164.1532, found 164.1524.

2-Trideuteriomethylbicyclo[4.4.0]dec-1-en-10-one. To a solution of bicyclo-[4.4.0]decane-2,10-dione (1.0 g, 6 mmol) in 10 mL of anhydrous diethyl ether under argon at 0 °C, methyl-*d*$_3$-magnesium iodide (18 mL, 1.0 M in diethyl ether, 18 mmol, Aldrich, 99 atom % D) was added dropwise. After being warmed to room temperature, the reaction mixture was stirred overnight, then quenched with saturated aqueous NH_4Cl, neutralized with aqueous HCl (10%), and then extracted with diethyl ether (2 × 30 mL). The combined extracts were washed with water, dried over anhydrous Na_2SO_4, filtered, and concentrated. The residue was dissolved in 40 mL benzene in a 100-mL, round-bottomed flask fitted with a Dean−Stark device. *p*-Toluenesulfonic acid (0.2 g) was added, and the mixture was heated under reflux for 2 h. After being cooled to room temperature, the reaction mixture was washed successively with saturated aqueous $NaHCO_3$, water, and brine. The organic phase was dried over anhydrous Na_2SO_4, filtered, concentrated, and subjected to column chromatography (silica gel, hexane-diethyl ether: 15:1) to give 0.47 g (47%) of 2-trideuteriomethylbicyclo[4.4.0]dec-1-en-10-one as a pale-yellow oil: ^{1}H NMR 1.18−1.27 (m, 1H), 1.32−1.48 (m, 2H), 1.67−1.76 (m, 2H), 1.84−2.00 (m, 3H), 2.07−2.17 (m, 2H), 2.25−2.34 (m, 2H), 2.46−2.52 (m, 1H); ^{13}C NMR 21.53, 23.94, 31.02, 33.19, 33.91, 39.34, 43.17, 135.08, 143.50, 204.61.

2-Trideuteriomethyl-10-methylenebicyclo[4.4.0]dec-1-ene (1′). Methyllithium (9.4 mL, 1.6 M solution in diethyl ether, 15 mmol, Aldrich) was added dropwise to a suspension of bis-cyclopentadiene titanium dichloride (1.74 g, 7.0 mmol) in 5 mL anhydrous diethyl ether under argon at 0 °C. After 1 h, the mixture was quenched with water. The ether layer was separated, dried over anhydrous Na_2SO_4, filtered, and concentrated. The resulting orange crystals were dissolved in 15 mL of anhydrous toluene, and 2-trideuteriomethylbicyclo [4.4.0]dec-1-en-10-one (0.4 g 2.4 mmol) in 5 mL of anhydrous toluene was added under argon. The reaction mixture was stirred at 70 °C in the dark for 40 h and cooled to room temperature. Addition of hexane produced a precipitate, which was removed by filtration. Concentration gave a crude product, which was subjected to column chromatography (basic aluminum, hexane), and a final purification by GC on the preparative column at 66 °C to afford 0.17 g (42.9%) of 2-trideuteriomethyl-10-methylenebicyclo[4.4.0]dec-1-ene as a colorless oil: ^{1}H NMR (500 MHz, benzene-*d*$_6$) 1.07−1.14 (m, 2H), 1.38−1.49 (m, 2H), 1.56−1.60 (m, 1H), 1.66−1.72 (m, 3H), 1.89−1.92 (m, 2H), 1.99−2.05 (m, 2H), 2.27−2.31 (m, 1H), 4.77 (q, J = 1.47 Hz, 1H), 5.00 (d, J = 2.44 Hz, 1H); ^{13}C NMR (benzene-*d*$_6$) 22.05, 27.73, 31.92, 32.49, 35.56, 37.41, 39.82, 111.12, 127.17, 135.75, 148.24; exact mass HRMS (EI) calcd for $C_{12}H_{15}D_3$ 165.1594, found 165.1586.

Kinetics. All analyses were by ^{1}H NMR in benzene-*d*$_6$ at 600 MHz on a Unity/Varian Inova 600 instrument. Even with this resolving power, baseline separation of the isotopomers in Figure 2 was not always achievable. To better separate the two sets of three signals used in the acquisition of the data-relating concentration and time of reaction (Table 2), the data were processed by using resolution enhancement by 1.0 Hz and Gauss apodization by 0.4 s. Samples were prepared by placement in NMR tubes with benzene-*d*$_6$ as the solvent and by being sealed under vacuum after three freeze-dry cycles. Heating was in the vapors of boiling liquids: acetophenone, average temperature: 201.6 ± 0.2 °C; diethyl oxalate, 184.42 ± 0.24 °C; *tert*-butylbenzene, 167.7 ± 0.2 °C. At 201.6 °C, two sets of NMR measurements were obtained at 15 time intervals ranging from 0.5 and 1.0 h at the beginning of a run to 110 and 205 h, respectively, at the end. A similarly large number of points was taken at the other temperatures. Acquisition times were 4.00 s; relaxation time delay was 40 s; and the number of accumulated determinations was 16.

To confirm that the borosilicate glass of the NMR tubes used as reaction vessels was not interfering with accuracy by acid-catalysis of undesired constitutional changes, two experiments were conducted in soft-glass tubes using *p*-xylene-*d*$_{10}$ as solvent at 201.6 °C for 112 h (403 200 s) and 205 h (738 000 sec). Analysis of compounds **1**, **2**, and (*E* + *Z*)-3 (See Figure 2), as described above, revealed concentrations that did not differ from the comparable runs in NMR tubes within experimental uncertainties: i.e., ±5% (Table SI-6).

Analysis of the kinetics of the rearrangement of compound **1′** requires correction for a weak absorption (∼11%) at 1.76 ppm (see uncorrected data in Table SI-4). A simple correction is made on the assumptions that the impurity is dideuteriomethyl **1** formed by partial exchange of deuterium by hydrogen during the preparation of 2-methylbicyclo[4.4.0]-dec-1-en-10-one, and that its contributions to the raw data at the various times of reaction can be calculated[30] on the basis of the approximate rate constants obtained for compound **1**. These values are then subtracted to produce the corrected values in Table SI-5. The resulting specific rate constants are those given in Table 3.

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Supporting Information Available: Seven tables giving concentration/time data. This material is available free of charge via the Internet at http://pubs.acs.org.

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