

Degenerate thermal isomerizations of *Z*-ethylidene-2-methylcyclobutane[†]

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ABSTRACT: The stereochemical and mechanistic aspects of the degenerate thermal isomerizations available to deuterium-labeled *Z*-ethylidene-2-methylcyclobutanes remain incompletely defined. Relevant data and several conjectural readings of the data are reconsidered in light of current understandings of thermal stereomutations and [1,3] carbon sigmatropic shifts. Copyright © 2006 John Wiley & Sons, Ltd.

KEYWORDS: thermal rearrangements; methylenecyclobutanes; conformationally flexible diradicals

INTRODUCTION

The stereochemical characteristics of [1,3] carbon sigmatropic shifts have become better and better understood over the past several decades, thanks to more successful experimental deconvolutions of reaction stereochemical complexities, better calculations of potential energy surfaces, and more powerful treatments of non-statistical dynamic effects.¹ Yet one early study of degenerate isomerizations involving a set of eight deuterium-labeled *Z*-ethylidene-2-methylcyclobutanes has remains unclarified.² The present contribution summarizes the published experimental data that led to conflicting views of reaction mechanism for this system, comments on some data reduction issues, and reconsiders likely determinants of reaction stereochemistry and mechanism.

RESULTS

Incomplete but still illuminating stereochemical information on the isomerizations shown by a methylenecyclobutane system, *Z*-ethylidene-2-methylcyclobutane, was reported in 1972–1973.² A kinetic study of structural isomerizations interconverting *E*- and *Z*-ethylidene-2-methylcyclobutane and *cis*- and *trans*-1-methylene-2,4-dimethylcyclobutane revealed a substantial preference, about 10:1, for methyl groups at C2 to rotate away from C3 as the C2–C3 bond was cleaved to initiate a [1,3] carbon migration. *Z*-Ethylidene-2-methylcyclobutane labeled with deuterium at C α equilibrated with the 2-*d*

labeled isotopomer much faster than it rearranged structurally, thus suggesting that it could serve as a useful system for detailed studies of the stereochemical aspects of degenerate isomerizations. Further, the rate of this deuterium scrambling was found to be larger than the rate of racemization of a non-racemic sample. Since antarafacial [1,3] carbon shifts transpose a deuterium label between C α and C2 without changing absolute stereochemistry at C2, while suprafacial shifts occur with a reversal of *R* and *S* stereochemistry at C2, this comparison of rate constants indicated a non-trivial participation of [1,3] antarafacial carbon shifts.

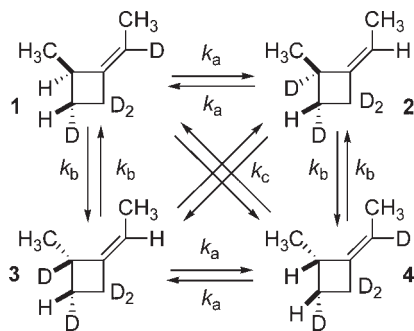
The most detailed data were secured through synthesizing a racemic *d*₄-labeled version of this hydrocarbon (**1**) and following the gas-phase thermal equilibrations among the isomers **1**, **2**, **3**, and **4** at 332°C (Scheme 1). Following thermal reactions the mixture of isomers **1–4** was purified by preparative GC and analyzed using ¹H-NMR spectroscopy at 100 MHz. The kinetic situation outlined in Scheme 1 features 12 rate constants but only three independent variables: all four horizontal arrows for the reactions shown are defined by rate constant *k*_a, all four vertical arrows by *k*_b, and all four diagonal arrows by *k*_c. The values for these rate constants reported in 1973 were *k*_a = 1.36, *k*_b = 0.40, and *k*_c = 0.86, all × 10⁻⁵ s⁻¹.²

The interconversions of the eight-isomer system (**1–4**, and their enantiomers) are defined by seven independent rate constants, for one-center stereomutations at C2 or at C3 (*k*_{2e}, *k*_{3e}), for two-center stereomutations at C2 and C3 simultaneously (*k*_{23e}), and four distinct [1,3] carbon shift reactions, resulting in *suprafacial*, *inversion* or *antarafacial*, *retention* or *suprafacial*, *retention* or *antarafacial*, *inversion* outcomes (*k*_{si}, *k*_{ar}, *k*_{sr}, *k*_{ai}).

The relationships expressing the three experimentally accessible parameters of Scheme 1 in terms of six of the seven stereochemically revealing rate constants, and the

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Scheme 1

measured values of the rate constants, are as follows:

$$k_a = k_{ar} + k_{si} = 1.36 \times 10^{-5} \text{ s}^{-1} \quad (1)$$

$$k_b = k_{sr} + k_{ai} = 0.40 \times 10^{-5} \text{ s}^{-1} \quad (2)$$

$$k_c = k_{2e} + k_{3e} = 0.86 \times 10^{-5} \text{ s}^{-1} \quad (3)$$

Thus the balance between the Woodward–Hoffmann ‘allowed’ and ‘forbidden’ paths for the [1,3] shifts was found to be 1.36:0.40 or 77:23, and one-center stereomutations ($k_{2e} + k_{3e}$) were very much in evidence. Another instance of a prominent role for stereomutation at C2 (through $k_{2e} + k_{23e}$) was uncovered when non-racemic 1-methylene-2-methylcyclobutane was heated at 333°C: the rate of racemization was much faster than the rate of isomerization to ethylidenecyclobutane.²

Two data sets for racemizations of non-racemic *Z*-ethylidene-2-methylcyclobutanes were secured. Non-racemic samples of *Z*-ethylidene-2-methylcyclobutane ((–)-**1**–*d*₀) and of (–)-**1** (of substantially higher optical activity) were prepared through selective destructions of racemic **1**–*d*₀ and of **1** using an optically active hydroborating reagent, and the kinetics of racemization at 332°C were determined polarimetrically. For the *d*₀ system, $k_\alpha = (4.93 \pm 1.13) \times 10^{-5} \text{ s}^{-1}$; for (–)-**1**, $k_\alpha = (4.12 \pm 0.46) \times 10^{-5} \text{ s}^{-1}$. Thus an additional parameter relating an observable with stereochemically informative rate constants was obtained, one dependent on suprafacial [1,3] shifts and on epimerizations at C2.

$$\frac{k_\alpha}{2} = k_{si} + k_{sr} + k_{2e} + k_{23e} = 2.06 \times 10^{-5} \text{ s}^{-1} \quad (4)$$

Unfortunately, experimental limitations of several sorts made it impossible to draw definitive conclusions. The k_a , k_b , and k_c rate constants, derived from data secured by planimeter integrations of C3 proton absorptions, were comparable with each other, but they could not be compared reliably with rate constants for deuterium-scrambling obtained with other samples at other times and based on analyses using different methods.³ These deficiencies could be readily overcome with the more

powerful analytical techniques available today, but a fundamental insufficiency would still remain. The experimental design framing the investigation could not provide a full reading of reaction stereochemistry and mechanism: four experimentally observed kinetic parameters, however accurately and precisely determined, can never give unique values for seven individual rate constants. The 77:23 balance between ‘allowed’ and ‘forbidden’ paths for [1,3] shifts and the fact that thermal stereomutations are of kinetic significance were plain, but the conjecture² that there might be substantial participation of antarafacial [1,3] shifts proved to be more provocative than convincing.

In 1976 this kinetic work was vigorously challenged: the responding publication reacted strongly to the possibility that there could be an antarafacial [1,3] carbon sigmatropic shift, and provided two detailed mechanistic rationales for [1,3] shifts with up to 100% suprafacial stereochemistry.⁴ It prompted the review literature to vent a sigh of relief: the later work was recognized for showing that the unlikely antarafacial shift was not in fact significant, or at least that the experimental data was consistent with little.⁵ And there the matter has rested, unresolved and unpursued through any fresh experimental efforts, since 1976.

It now seems time to comment on the reinterpretation⁴ of the kinetic data published in 1972–1973² and on the mechanistic models proposed.⁴ Revisiting this work provides an instructive appreciation of how such isomerizations were conceptualized and modeled 30 years ago, and has prompted a fresh mechanistic perspective on the thermal isomerizations of methylenecyclobutanes.

DATA REDUCTIONS

Kinetic data are invariably reduced to rate constants through some fitting procedure, and different procedures may well give different values for the same rate constants. The distinctions may be modest or of real importance.

The data used to calculate rate constants k_a , k_b , and k_c of Scheme 1 were reevaluated using Runge–Kutta integrations, and some rate constants differing by a factor of 50% from those previously reported were obtained.⁴ The new values were $k_a = 1.6$, $k_b = 0.6$, and $k_c = 0.6$, all $\times 10^{-5} \text{ s}^{-1}$, rather than the original values $k_a = 1.36$, $k_b = 0.40$, and $k_c = 0.86$, all $\times 10^{-5} \text{ s}^{-1}$.

One might have imagined that a superior data-reduction methodology had been employed, that the new rate constants derived were more faithful to the experimental data, and accordingly that the completely altered interpretation of reaction stereochemistry which was advanced merited acceptance.

Runge–Kutta methods for numerical integrations are powerful tools for treating systems of differential equations, especially when exact integrated solutions

are not easily available. They can approximate the values obtained analytically with wonderful reliability, but they can never provide better values.

In the present case, the kinetic situation of Scheme 1 is defined by the set of differential equations given in Eqns (5)–(8), where $k = (k_a + k_b + k_c)$.

$$\frac{-d(1)}{dt} = k(1) - k_a(2) - k_b(3) - k_c(4) \quad (5)$$

$$\frac{-d(2)}{dt} = -k_a(1) + k(2) - k_c(3) - k_b(4) \quad (6)$$

$$\frac{-d(3)}{dt} = -k_b(1) - k_c(2) + k(3) - k_a(4) \quad (7)$$

$$\frac{-d(4)}{dt} = -k_c(1) - k_b(2) - k_a(3) + k(4) \quad (8)$$

An exact integrated solution of this set of equations is easily obtained; the linear algebra programs provided in Maple software⁶ were employed, but other methods would lead to the same results. The integrated rate expressions for isomers **1**, **2**, **3**, and **4** and the experimentally determined initial concentrations (**1** = 91.6%; **4** = 8.4%)² are as given in Eqns (9)–(12).

$$\begin{aligned} 1(t) = & 25.0 + 25.0 * \exp(-2(k_a + k_b)t) \\ & + 20.8 * \exp(-2(k_a + k_c)t) \\ & + 20.8 * \exp(-2(k_b + k_c)t) \end{aligned} \quad (9)$$

$$\begin{aligned} 2(t) = & 25.0 - 25.0 * \exp(-2(k_a + k_b)t) \\ & - 20.8 * \exp(-2(k_a + k_c)t) \\ & + 20.8 * \exp(-2(k_b + k_c)t) \end{aligned} \quad (10)$$

$$\begin{aligned} 3(t) = & 25.0 - 25.0 * \exp(-2(k_a + k_b)t) \\ & + 20.8 * \exp(-2(k_a + k_c)t) \\ & - 20.8 * \exp(-2(k_b + k_c)t) \end{aligned} \quad (11)$$

$$\begin{aligned} 4(t) = & 25.0 + 25.0 * \exp(-2(k_a + k_b)t) \\ & - 20.8 * \exp(-2(k_a + k_c)t) \\ & - 20.8 * \exp(-2(k_b + k_c)t) \end{aligned} \quad (12)$$

With these explicit functions, the best values for the parameters may be found quickly with the computational assistance of the 'Solver' tool within the widely available Microsoft Excel program, by minimizing the root mean square (rms) deviation for calculated *versus* observed concentrations for all 24 data points obtained through the six kinetic runs.² The parameters found through this approach were $(k_a + k_b) = 1.755E-5$, $(k_a + k_c) = 2.221E-5$, and $(k_b + k_c) = 1.256E-5$, and hence $k_a = 1.36$, $k_b = 0.40$, and $k_c = 0.86$, all $\times 10^{-5} s^{-1}$. The calculated rms deviation was 1.7%.

If the initial concentrations are postulated to be **1** = 90% and **4** = 10%,⁴ the coefficients of the integrated rate expressions (Eqns (9)–(12)) will be slightly different:

the third and fourth coefficients in the integrated expressions for **1**(*t*), **2**(*t*), **3**(*t*), and **4**(*t*) change from 20.8, 20.8 to 20.0, 20.0, with the same pattern of plus and minus signs. Calculations of the best parameters using the exact integrated solutions of Eqns (5)–(8) for **1**(*t*), **2**(*t*), **3**(*t*), and **4**(*t*) and the 'Solver' program lead to $(k_a + k_b) = 1.761E-5$, $(k_a + k_c) = 2.097E-5$, and $(k_b + k_c) = 1.162E-5$. Thus the rate constants change to $k_a = 1.35$, $k_b = 0.41$, and $k_c = 0.75$, all $\times 10^{-5} s^{-1}$. Adjusting the initial concentrations leads to a small reduction of the rms deviation, to 1.6%, while only one of the three rate constants (k_c) changes significantly, diminishing by 13%. The parameters k_b and k_c remain quite unequal.

When the set of rate constants $k_a = 1.6$, $k_b = 0.6$, and $k_c = 0.6$ (all $\times 10^{-5} s^{-1}$) and the initial concentrations **1** = 90% and **4** = 10% are used to calculate the 24 theory-based concentrations, the rms deviation increases to 2.4%. The 2.4/1.7 increase in the rms deviation is not trivial. Runge–Kutta methods were used to calculate theoretical functions based on the assigned rate constants $k_a = 1.6$, $k_b = 0.6$, and $k_c = 0.6$ (all $\times 10^{-5} s^{-1}$) and the initial concentrations **1** = 90% and **4** = 10%.⁴ These constants were 'found to give a reasonable fit to the data,' but they were not determined through a search for the optimum values for the kinetic parameters, through iterative Runge–Kutta calculations or any other approach. It was emphasized 'that the new values of k_a , k_b , and k_c are not unique. They are no better than the original values, but they do allow an interpretation of the reaction that appeals to precedence and steric reasonableness.'⁴ That suitability may have been decisive.

One knows full well that fourth-order (and other) Runge–Kutta methods are frequently used because computer programs implementing them are readily available, but such programs often have severe limitations, especially when they provide no interface to some optimization method. Finding the best set of rate constants with such programs can be a difficult and tedious task.⁷

Ironically, Fleming's data reduction approach depended on Runge numerical integration techniques and a Monte Carlo optimization strategy to find the three kinetic parameters which would minimize the rms deviation.³ He did not have access to the conveniently available software tools for data reduction taken for granted today, but his values for k_a , k_b , and k_c still appear to give the best fit to the experimental data.

DISCUSSION

The two detailed models for the thermal reactions accessible to (2R)–**1** were outlined.⁴ Each featured a 36:64 branching between a concerted Woodward–Hoffmann 'allowed' *suprafacial*, *inversion* [1,3] carbon shift and the generation of a diradical intermediate.

In the first model, the diradical intermediate gave products in a stereorandom fashion. Thus 64/8 proportional contributions to products consistent with all four possible [1,3] shifts, all three modes of stereomutation, and reversion to (2*R*)-**1** were predicted through this model. According to the model, $k_{si} \propto 44$, and k_{ar} , k_{ai} , k_{sr} , k_{2e} , k_{3e} , and k_{23e} are all equal and $\propto 8$. The $(k_{si} + k_{sr})$: $(k_{ar} + k_{ai})$ ratio, 52:16, indicated that 24% of all [1,3] shifts occurred antarafacially, a larger proportion than the minimum of 16% suggested earlier.² If the proportionality were set by taking $k_a = (k_{ar} + k_{si}) = 1.36 \times 10^{-5} \text{ s}^{-1}$ (experimental) to be equal to the predictions of the model, then the other rate constants would be $k_b = 0.42$, $k_c = 0.42$, and $k_{\alpha}/2 = 1.78$ (all $\times 10^{-5} \text{ s}^{-1}$).

In the second model, the diradical is formed through a 'bevel' rotation in one defined sense, increasing the C3—C4—C1—C2 dihedral angle as the C2—C3 bond breaks; the methyl group at C2 moves outward, diminishing the CH₃—C2—C1—C α dihedral angle. The diradical in this model loses stereochemistry at C3, and thus the 64 proportional contributions to products are divided among only four options. One leads back to (2*R*)-**1**, and the three new isomers are formed so that $k_{si} \propto (36 + 16)$, $k_{sr} \propto 16$, and $k_{3e} \propto 16$. The rate constants k_{2e} , k_{23e} , k_{ar} , and k_{ai} are all defined to be zero. Taking $k_{si} = k_a = 1.36 \times 10^{-5} \text{ s}^{-1}$, the other kinetic parameters are predicted to be $k_b = 0.42$, $k_c = 0.42$, and $k_{\alpha}/2 = 1.78$ (all $\times 10^{-5} \text{ s}^{-1}$).

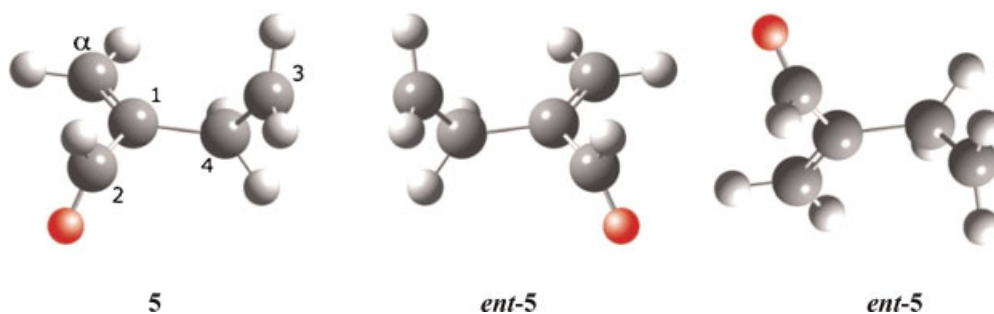
Of particular note is the dual utilization in both models of the k_{si} symbol to represent both a Woodward–Hoffmann 'allowed' reaction, one with a definite transition structure, and again to label another contribution to the same product formed through a stereorandom diradical intermediate.⁴ Both uses of k_{si} are perfectly valid, though confusions can easily arise. The distress felt by some when the possibility of an antarafacial [1,3] shift component was raised in 1972–1973 may have stemmed in part from assuming that a k_{ar} product had to be formed through a geometrically awkward 'allowed' and concerted [1,3] *ar* shift. When used to denote product stereochemistry, relative to the stereochemistry of starting material, the rate constant symbols k_{si} , k_{ar} , k_{sr} , and k_{ai} imply nothing about mechanism or transition structure, nor should any be assumed. This point is obvious today; many instances of rigorously documented antarafacial

[1,3] carbon shifts are known. Mechanistically significant conformationally flexible short-lived diradical intermediates make such [1,3] carbon shifts possible.

Any blend of the two models offered in 1976⁴ would leave all predicted relative values of the accessible kinetic parameters the same, with $k_b = k_c$, contrary to the experimental values. The second model, with k_{2e} and k_{23e} equal to zero, seems particularly problematic. Nevertheless, these models serve very well to underscore the complexity of the kinetic situation and the generally inadequate experimental and theoretical grounds at that time for formulating intellectually coherent mechanistic readings of the stereomutations and [1,3] shifts observed for methylenecyclobutanes.

It has been reasonably clear from the earliest thoughtful considerations of thermal isomerizations of methylenecyclobutanes that they probably take place through diradical intermediates.^{8,9} For methylenecyclobutane, the parent system, the most detailed published theory has confirmed this view and found that a conformationally flexible diradical intermediate is formed through three consecutive processes.¹⁰ The C2—C3 bond stretches, then clockwise rotation about the C1—C4 bond leads to a transition structure of C₁ symmetry (**5**) in which very little rotation about C1—C2 or C3—C4 has taken place. (One hydrogen in **5** in Scheme 2 has been highlighted, to aid in visualizing the perspective.) The C2 methylene group is perpendicular to the plane of the C1=C α double bond and C3 is far removed from C α ; the C2—C1—C4—C3 dihedral angle is calculated to be 67.2°. The C2—C1—C4 and C1—C4—C3 bond angles are 116 and 112.2°. Finally, rotation about C1—C2 leads to stabilization of the diradical intermediate as an allyl radical functionality is generated. The diradical thus generated, a 2-methylenebutan-1,4-diyl, or a homotrimethylenemethane,¹¹ is about 12–14 kcal/mol more stable than the transition structure, depending upon the geometrical details at C3. Rotation about the C3—C4 bond is virtually free.¹⁰

Rotation about C1—C4 leading from methylenecyclobutane to **5** can take place in both senses: if the change in the C2—C1—C4—C3 dihedral angle corresponds to a counter-clockwise rotation, the mirror image of **5**, *ent-5*, will be formed. The views of **5** and *ent-5* at the left and center of Scheme 2 emphasize the enantiomeric



Scheme 2

relationship. The views of **5** and *ent-5* at the left and right of Scheme 2 emphasize the clockwise *versus* counter-clockwise rotations about C1—C4.

Progress along the reaction coordinate leading from the diradical intermediate to a transition structure **5** or *ent-5* will involve rotation about C2—C1 to locate the C2-methylene function perpendicular to the plane of the C1=C α double bond before any substantial change in C2—C1—C4 or C1—C4—C3 bond angles take place.

Now if this basic model connecting methylenecyclobutane with **5** and *ent-5* and on to the 2-methylenebutan-1,4-diyl diradical were qualitatively suitable for considering the thermal reactions of deuterium-labeled *Z*-ethylidene-2-methylcyclobutanes, with C2-methyl rotating away from C3 following clockwise or counter-clockwise rotations about C1—C4, a given starting material such as (2*R*)-**1** would lead to two families of diradicals, having the C3-methylene group on different faces of the allylic function. A diradical could combine with the allyl function at either end, and with either stereochemistry. The C2—C1 (or equivalent C α —C1) rotations in diradical intermediates would have dominant influences on the relative rates of epimerizations at C2 and of suprafacial *versus* antarafacial [1,3] shifts. The net stereochemical outcomes would be dictated by the sense of rotation away from planarity of the original C2 or C α -ethylidene groups in a diradical, relative to the position of the C3-methylene group, not on orbital symmetry considerations. The overall picture would be one of considerable complexity based on conformational issues and multiple options for the various components of the reacting system, but there would be only two basic transition structures (ignoring the precise labeling details) involved. These diastereomeric transition structures and reaction dynamics would mediate all stereomutation and [1,3] shift processes. The stereochemical outcomes would depend on the relative senses of rotation about C1—C2 and of rotation about C1—C4. If both options were utilized, both suprafacial and antarafacial [1,3] shifts would occur.

This hypothetical picture may well help frame future experimental attempts to pin down reaction stereochemistry through determinations with good precision and accuracy rate constants for all seven net isomerizations that may occur when (–)-**1**, or a similar isotopically labeled non-racemic methylenecyclobutane, is heated. Theory-based efforts to test the proposition that two distinct paths may lead from a *Z*-ethylidene-2-methylcyclobutane to diastereomeric transition structures and thence to substituted 2-methylenebutan-1,4-diyl diradicals may be envisaged. The extent to which a diradical as first generated

finds an exit channel and forms a stereomutation product or a [1,3] shift product before relaxing to a more stable diradical enjoying a full 12–14 kcal/mol of π -electron delocalization energy, or forms a new bond at C3 before it has time for C2 and C α to become equivalent, could also be addressed through dynamics calculations.

Both experimentalists and theoreticians still have work to do before degenerate isomerizations of methylenecyclobutanes can be considered well understood. Both efforts are anticipated to be very challenging and very rewarding.

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