200 W) arranged symmetrically in the walls of the aluminum block. Four of the heaters were controlled by a precision temperature controller (Model 253, Bailey Instrument Co., Danville, Calif.), and the other four were controlled with a Variac.

The temperature was measured to 0.3° using an uncalibrated chromel alumel thermocouple connected to a potentiometer (Rubicon Co., Philadelphia, Pa). Early work was done using a thermocouple inserted into the aluminum block. A thermocouple in the aluminum block and one protruding into the reaction vessel both showed identical temperatures at a given time.

The aluminum block was housed in a box 34 × 34 × 18 cm. Four pieces of refractory firebrick were placed in the corners of the box such that the aluminum cylinder rested on the corners of the firebricks with as little contact area as possible. The box was packed with diatomaceous earth (swimming pool filter aid) as insulation.

Samples were introduced into the reactor as gases by expansion from a ballast bulb, and were retrieved using the method in reverse; that is, expansion from the reactor into the ballast bulb. The reaction times were noted, and the samples were condensed using liquid nitrogen and subjected to the appropriate analytical technique.

Starting materials (**7** or **8**) used to study the interconversions of isomers **7**–**10** were introduced into the reactor at 7–10 Torr. The temperature measured by thermocouple in the aluminum heating block was 332°. The product mixtures were condensed and diluted with pentane (10 μl), and were analyzed by glpc on column B. The data are recorded in Tables II and III and Figures 2 and 3.

Thermal rearrangement of deuterium-labeled substrates **7**-α-*d* and **8**-α-*d* at 332° at pressures of about 18 Torr, followed by glpc on column B to isolate the right geometrical isomer and analysis for deuterium distribution by nmr spectroscopy, led to the data given above in Tables IV and V and plotted in Figure 4.

Rate Constant Determinations. To find the best estimations of first-order rate constants, a fourfold sequence of operations was performed iteratively. First, each rate constant was estimated or guessed. Second, concentrations of isomers **7**–**10** were computed as functions of time from these rate constants. Third, the calculated concentrations were compared with experimentally determined concentrations. Fourth, the process was repeated with different sets of rate constants. This iteration proceeded until the best fit, defined as that which gave the smallest sum of squared deviations between calculated and observed concentration values, was found.

Initial rates and equilibrium concentrations were helpful guides to prudent selection of trial rate constants. With a given set of rate constants, concentrations of the four hydrocarbons as a function of time were calculated from the appropriate differential equations using Runge numerical integration. The mole fraction X was evaluated according to $X(t + \Delta t) = X(t) + \mathrm{f}[X(t) - (X(t - \Delta t) - X(t))/2]\Delta t$ where Δt is a small time increment. The new value of X was then used to calculate a subsequent value at time $t + 2\Delta t$, and the process was repeated to cover the time span of interest.

In trial calculations, Δt values of 1, 5, and 20 min gave values for the system A → B → C ($k_1 = 2 \times 10^{-5}$, $k_2 = 1 \times 10^{-5}$ sec^{-1}) differing from the exact solutions to the integrated rate expressions by at most a few parts per 10,000.

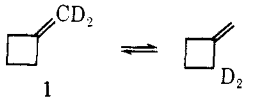
Thermal Rearrangements of Methylenecyclobutanes. Degenerate Rearrangement of (Z)-1-Ethylidene-2-methylcyclobutane with Antarafacial Allylic Participation[1]

John E. Baldwin* and Ronald H. Fleming[2]

Contribution from the Department of Chemistry, University of Oregon, Eugene, Oregon 94703. *Received February 12, 1973*

Abstract: Optically active (*Z*)-1-ethylidene-2-methylcyclobutane racemizes at 332° more slowly than (*Z*)-1-(1-deuterioethylidene)-2-methylcyclobutane equilibrates with (*Z*)-1-ethylidene-2-deuterio-2-methylcyclobutane. This result requires that at least some of the 1,3-carbon migration in the degenerate methylenecyclobutane isomerization occurs with antarafacial allylic participation. Optically active 1-methylene-2-methylcyclobutane at 333° is isomerized to its enantiomer faster than it is converted to 1-ethylidenecyclobutane, thus demonstrating thermal epimerization at C(2) without carbon migration.

The methylenecyclobutane system exhibits thermal automerization through a 1,3-sigmatropic migration of carbon (**1** ⇌ **2**).[3,4]


1 **2**

There are just four possible stereochemical outcomes for a 1,3-carbon shift, the combinations of retention or inversion at the migrating carbon, and suprafacial or antarafacial utilization of the allylic moiety. The orbital-symmetry-allowed combinations are the retention-antarafacial (ra) and inversion-suprafacial (is) modes. The retention-suprafacial (rs) and inversion-antarafacial (ia) stereochemical outcomes are disallowed.[5,6]

1,3-Sigmatropic carbon shifts similar to the one responsible for the degenerate methylenecyclobutane isomerization are well known in other systems: the vinylcyclopropane to cyclopentene isomerization,[7-13]

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[1] Supported by the National Science Foundation and Hoffmann-La Roche, Inc.

[2] National Science Foundation Predoctoral Trainee, 1968–1972.

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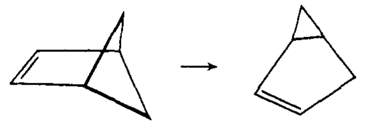
[13] R. A. Clark, *Tetrahedron Lett.*, 2279 (1971).

and the reverse process, as in the isomerization of bicyclo[2.1.1]hexenes to bicyclo[3.1.0]hexenes,[14–17] have been studied in great detail; yet many stereochemical points remain unclear, either because the stereochemical integrity of a starting material is lost faster than the isomerization being studied occurs, or because geometrical constraints dictate the stereochemical outcome. Among these studies one may find many examples of migration with inversion and migration with retention in a suprafacial sense across the face of an allylic system.

Kinetic studies on two of these isomerizations, one (**3** → **4**) which may be presumed to occur with inversion,[14] and one (**5** → **6**) which has to proceed with retention, lead to determinations of equal activation energies (35.2 and 35.3 kcal/mol, respectively).[18,19]



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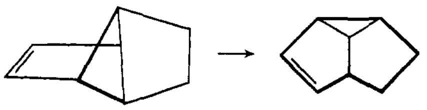


5 6

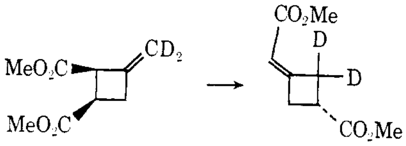
The vinylcyclobutane to cyclohexene rearrangement has been observed less frequently,[20,21] but some detailed stereochemical studies have been made most notably in the isomerizations of bicyclo[2.1.1]hexenes.[14–17]

Divinylcyclobutanes rearrange to vinylcyclohexenes.[22–26] Most examples of this isomerization have been stereochemically uninformative,[22–25] but in the recent work of Berson and Dervan[26] some quantitative data on reaction stereochemistry have been gained: two isomers of *trans*-1,2-dipropenylcyclobutane were found to rearrange to 3-methyl-4-propenylcyclohexenes with the inversion-suprafacial and retention-suprafacial pathways predominating. Starting with the optically active *trans,trans*-dipropenyl isomer, and after a correction for racemization of starting material during the thermolysis, the optical rotations of the *cis*- and *trans*-3-methyl-4-*trans*-propenylcyclohexenes produced in a single run, the ratio of these hydrocarbons determined by glpc, and the values for the rotations of optically pure starting material and both products led to a dissection of reaction stereochemistry which included all four possible outcomes: 50.8% of the 1,3-carbon shift was is, 5.4% ra, 43.0% rs, and 0.8% ia.[26]

Thermolyses of bicyclo[3.2.0]heptene derivatives to bicyclo[2.2.1]hept-5-enes, as in the systems studied by Berson and coworkers,[26–29] have also given many instances of migration with retention or inversion with allylic participation in the suprafacial mode.

Other examples of isomerizations interpretable as involving 1,3-sigmatropic carbon shifts include the 2,5-bornadiene to 3,7,7-trimethylcycloheptadiene conversion[30] and the automerization of 2-methylene-5-norbornene.[31] In the first case, a stereochemical label becomes randomized at some point between reactant and product; in the second, no stereochemical data are available.

Only one stereochemical study on a substituted methylenecyclobutane system has been reported. Doering and coworkers[32] found that the (−)-1-dideuteriomethylene-*cis*-2,3-dicarbomethoxycyclobutane (**7**) gave a mixture of rearrangement products from which the (−)-antipode **8** was isolated by resolution; nmr spectroscopic analysis indicated the deuterium labeling shown. Thus, retention at the migrating center for that part of the reaction which gave the (−)-antipode of product was established.



7 8

The Doering study defined in one case the stereochemical outcomes at migration origin and at the migrating carbon. The most immediate specific need for additional stereochemical information of methylenecyclobutane automerizations, then, would seem to be localized at the migration terminus.

Other work on 1,3-carbon migrations has demonstrated the occurrence of two stereochemical outcomes, usually in systems giving the allylic unit no options. The most immediate general need for additional stereochemical information on 1,3-sigmatropic carbon shifts, then, is to begin work with molecules that do not geometrically preclude the other two reaction modes, retention-antarafacial and inversion-antarafacial, and that permit one to recognize these stereochemical outcomes when and if they do occur.

When our kinetic study of the equilibration of (*E*)- and (*Z*)-1-ethylidene-2-methylcyclobutanes and *cis*- and *trans*-1-methylene-2,4-dimethylcyclobutane gave rate constants which seemed inexplicable in terms of a conventional model based on hypothetical diradical intermediates, we directed our efforts toward a more thorough stereochemical study of one degenerate process: the automerization of (*Z*)-1-ethylidene-2-methylcyclobutane (**9** $\rightleftharpoons$ **10**). This molecule undergoes a 1,3-carbon migration with deuterium scrambling detectable by nmr spectroscopy so fast relative to the

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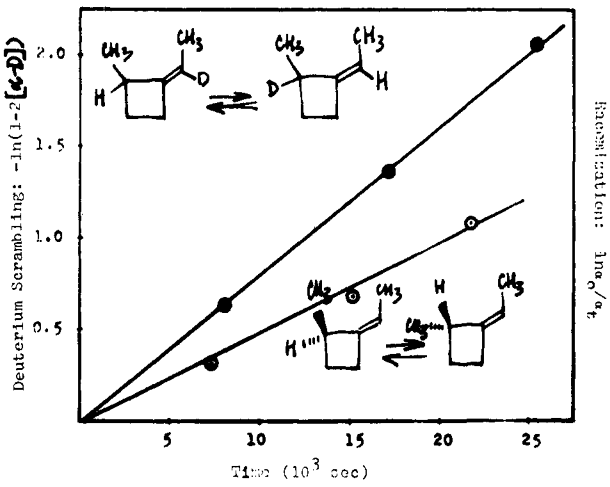
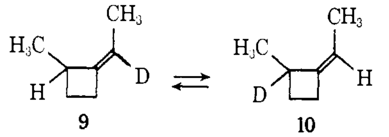


Figure 1. Kinetic plots for deuterium scrambling of (*Z*)-1-(1-deuterioethylidene)-2-methylcyclobutane (**9**)[33] and for racemization of (−)-(*Z*)-1-ethylidene-2-methylcyclobutane ((−)-**13**).

other modes of isomerization that the process may be treated as a simple two-component approach toward equilibrium.[33]

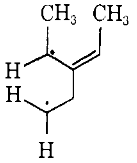


9 **10**

Resolution of this deuterium-labeled hydrocarbon would permit one to measure two different rate constants for approach to equilibrium: k_{ds}, the deuterium scrambling process giving eventually a 1:1 mixture of **9** and **10**, and k_{α}, the racemization of the system, giving eventually completely racemic material.

By comparing these two rate constants with predictions based on various mechanistic models, some inferences might be drawn.

Racemization without deuterium scrambling could be accomplished through direct epimerization[34] at C(2) or by way of a π-methylenecyclobutane,[35] or a diradical intermediate such as **11** in which C(α) and C(2) remained distinguishable. Racemization and deuterium scrambling at equal rates would be predicted for rearrangements through a diradical intermediate in which C(α) and C(2) were undistinguishable, either instantaneously as in **12** or on a time-averaged basis, *whatever the stereochemical modes for generation or collapse of such intermediates.*



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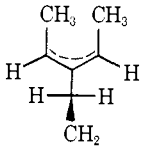

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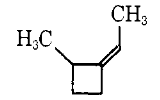
Mechanisms involving intermediates like **11** and **12**, then, can be invoked to rationalize all experimental outcomes in which $k_{\alpha} > k_{ds}$.

The allowed inversion-suprafacial mode would predict $k_{\alpha} = k_{ds}$, while the allowed retention-antarafacial path predicts $k_{\alpha} = 0$. The disallowed retention-suprafacial route predicts $k_{\alpha} = k_{ds}$, while the disallowed inversion-antarafacial possibility would require $k_{\alpha} = 0$.

Thus, an experimental result $k_{\alpha} < k_{ds}$ may be accommodated by 1,3-carbon migrations in which antarafacial allylic participation plays a roll at least proportionate to $(k_{ds} - k_{\alpha})/k_{ds}$. Any epimerization without migration would serve to minimize the antarafacial component inferred from a finding of $k_{\alpha} < k_{ds}$.

Results

I. Antarafacial Allylic Participation.[36] *rac*-(*Z*)-1-Ethylidene-2-methylcyclobutane[33] (**13**) was treated



13

with diisopinocamphylborane[37,38] derived from (−)-α-pinene. The recovered hydrocarbon, isolated by preparative glpc, had $[\alpha]^{27}_{222\,\mathrm{nm}}$ −870° in the gas phase.

The racemization rate was determined by heating samples of the levorotatory hydrocarbon for appropriate times at 332° in a glass reactor at about 10 Torr, then isolating this partially racemized *Z* isomer by glpc and measuring its rotation in the gas phase. The amount of hydrocarbon causing the observed rotation was determined by quantitative glpc, using added cyclohexene as an internal standard. The kinetic data are gathered in Table I, and plotted, together with the data for deuterium scrambling,[33] in Figure 1. The 95% confidence interval of the racemization rate, k_{α}, is 4.93 ± 1.13 × 10^{-5} sec^{-1}.

Table I. Kinetic Data for Racemization of (−)-(*Z*)-1-Ethylidene-2-methylcyclobutane at 332°

Reaction time (10^3 sec)	$[\alpha]^{27}_{222\,\mathrm{nm}}$ (deg)
0	−870
7.3	−632
15.2	−440
21.8	−294

Discussion

The experimental result places the 95% confidence intervals for $k_{\alpha} = 4.93 \pm 1.13 \times 10^{-5}$ sec^{-1} and for $k_{ds} = 8.15 \pm 0.60 \times 10^{-5}$ sec^{-1} well apart. Considering only random errors, the conclusion $k_{\alpha} < k_{ds}$ seems firm, and one may infer that at least 40% of the 1,3-sigmatropic carbon migration occurs with antarafacial allylic participation.

Yet one must exercise caution in interpretation. If

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(33) J. E. Baldwin and R. H. Fleming, *J. Amer. Chem. Soc.*, **95**, 5251 (1973).

(34) F. T. Smith, *J. Chem. Phys.*, **29**, 235 (1958).

(35) Compare π-cyclopropane proposals: R. Hoffmann, *J. Amer. Chem. Soc.*, **90**, 1475 (1968).

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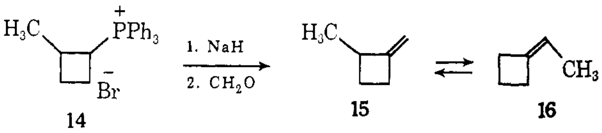
thermal epimerization at C(2) without carbon migration did transpire, more of the sigmatropic shift would be antarafacial with respect to the allylic component. If secondary deuterium kinetic or equilibrium isotope effects should happen to be significant, the estimated relative importance of the antarafacial component could be correspondingly inaccurate.

The first possibility, thermal epimerization at C(2) without migration, was investigated in another system: optically active 1-methylene-2-methylcyclobutane. This hydrocarbon would rearrange to inactive ethylidenecyclobutane. Any loss of optical activity faster than conversion to this product would have to be through epimerization at C(2).

II. C(2) Epimerization. The preparation of 1-methylene-2-methylcyclobutane was accomplished by a sequence similar to the one employed for the 1-ethylidene-2-methylcyclobutanes.[33] The purified intermediate 2-methylcyclobutyltriphenylphosphonium bromide (**14**) was converted to the corresponding ylide with sodium hydride in dry dimethyl sulfoxide. The Wittig reaction with gaseous formaldehyde gave a 12% yield of glpc-purified product **15**.



Thermolysis of 1-methylene-2-methylcyclobutane (**15**) at 333° gave ethylidenecyclobutane (**16**). The equilibrium ratio found, 0.477–0.523, is in fair agreement with the report of Flowers and Gibbons.[39] Even after more than 50 half-lives only 2% of unknown side products were formed.

Partial resolution of hydrocarbon **15** was achieved by selective destruction using diisopinocamphylborane.[37,38]

An improvement in technique for analyzing the partially racemized hydrocarbon was accomplished by measuring concentrations manometrically. In constructing the apparatus, two considerations had to be balanced: accuracy was to be maximized while the sample requirements were to be minimized. No exact precedents were uncovered in the literature, but ample guidance was found: manometer accuracy as well as the general theory and practice of mercury manometry have been exhaustively treated by the National Bureau of Standards.[40]

A manometer was constructed which could be attached directly to a 10-cm ORD cell, and which was volumetrically as small as possible (see Figure 2). In practice, sample was transferred to the cold trap, A, from the vacuum line using liquid nitrogen as coolant. The entire system was evacuated to less than 10^{-4} Torr, stopcocks B and C were closed, and the sample was allowed to come to thermal equilibrium with the surroundings. The difference in the height of the mercury levels was measured with a cathetometer, stopcock D was closed, the 1-dm ORD cell was removed at ball-and-socket joint E, and the optical rotation was measured. The cell was once again evacuated and a blank rotation was measured. Specific rotation was calculated using the ideal gas law and the net rotation. By combining constants and conversion factors, the following formula was obtained.

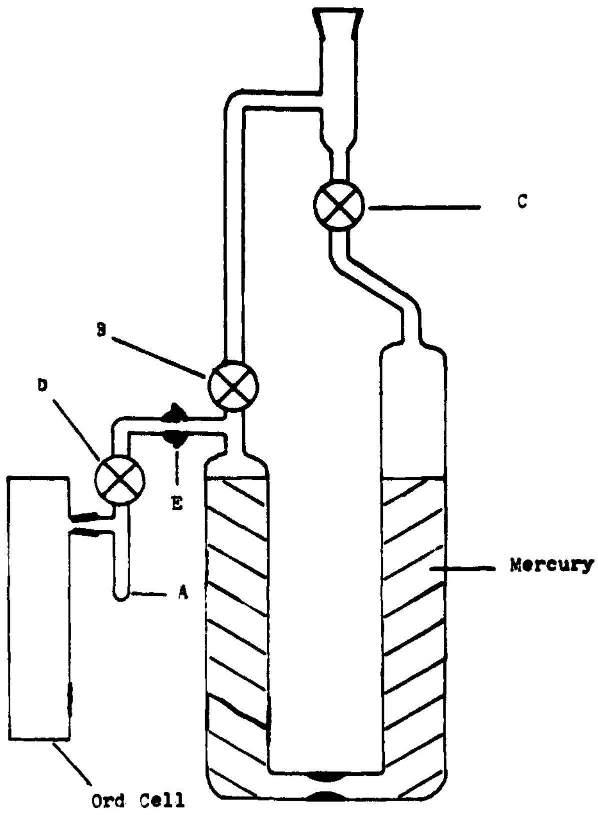


Figure 2. Cell for ORD measurements and mercury manometer.

$$[\alpha] = \frac{62{,}300T}{PM}\alpha$$

Here T is temperature in °K, P is pressure in Torr units, M is molecular weight in amu, and α is the measured rotation in degrees.

This procedure was used for following the kinetics of racemization of 1-methylene-2-methylcyclobutane. Samples of optically active **15** were pyrolyzed at 333° to yield **16** and partially racemized **15**. After each sample was retrieved from the vacuum line, it was subjected to glpc analysis using flame ionization detection to determine the proportions of **15** and **16**. Starting material was then purified by preparative glpc, and its specific rotation was determined in the gas phase using the manometric technique just described. The data obtained are shown in Table II.

Table II. Kinetic Data for Isomerization and Racemization of (+)-1-Methylene-2-methylcyclobutane ((+)-**15**) at 333°

Reaction time (10^3 sec)	Rel concn **15**	Rel concn **16**	$[\alpha]^{27}_{222\text{ nm}}$ (deg) **15**	$[\alpha]^{27}_{222\text{ nm}}$ (deg) (**15** + **16**)
0	1.00	0.0	193	193
1.94	0.875	0.125	102	89.0
3.83	0.795	0.205	57.5	45.7
5.64	0.723	0.277	32.4	23.4
7.59	0.673	0.327	16.0	10.8
300	0.477	0.523		

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(39) M. C. Flowers and A. R. Gibbons, *J. Chem. Soc. B*, 362 (1971).

(40) "Mercury Barometers and Manometers," National Bureau of Standards, Monograph 8, U. S. Government Printing Office, Washington, D. C., 1960.

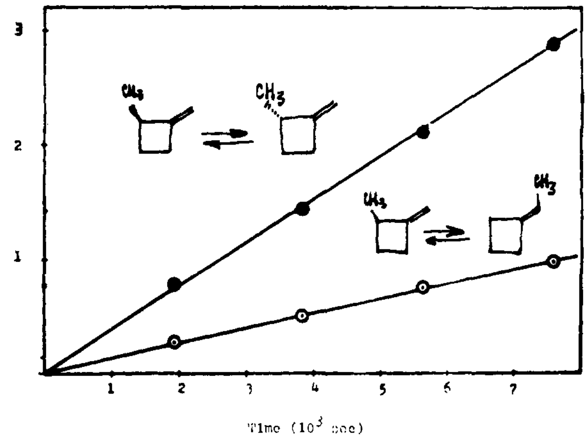

Figure 3. Kinetic plots for racemization (upper line) and of structural equilibration with 1-ethylidenecyclobutane (**16**) of (+)-1-methylene-2-methylcyclobutane ((+)-**15**).

The rate constant for total loss of optical activity, k_α, is equal to the rate constant for formation of ethylidenecyclobutane, k_1, plus twice k_2, the rate constant for formation of (−)-**15** from (+)-**15**.

$$\begin{tikzcd}
(+)\text{-}\mathbf{15} \arrow[rr, shift left, "k_2"] \arrow[dr, shift left, "k_1"'] & & (-)\text{-}\mathbf{15} \arrow[ll, shift left, "k_2"] \arrow[dl, shift left, "k_1"'] \\
& \mathbf{16} \arrow[ul, shift left, "k_{-1}"'] \arrow[ur, shift left, "k_{-1}"'] &
\end{tikzcd}$$

The total optical activity of the system was calculated from the specific rotations [α] for 1-methylene-2-methylcyclobutane samples and the relative concentration data. The 95% confidence interval for racemization was $k_\alpha = 37.7 \pm 1.6 \times 10^{-5}$ sec^{-1}. The 95% confidence interval for approach to structural equilibrium was $(k_1 + 2k_{-1}) = 12.9 \pm 0.9 \times 10^{-5}$ sec^{-1} (see Figure 3). From these values and the equilibrium ratios of **15** and **16** may be calculated $k_1 = 6.8 \times 10^{-5}$, $k_{-1} = 3.1 \times 10^{-5}$ sec^{-1}, and $k_2 = 15.5 \times 10^{-5}$ sec^{-1}.

An alternative but equivalent analysis of the isomerizations is possible, using the differential equations for the three-component system, which may be solved in closed form.[41]

Conclusions

The demonstration of facile thermal epimerization at C(2) of 1-methylene-2-methylcyclobutane strengthened the possibility that the 1,3-sigmatropic shift giving deuterium scrambling **9** $\rightleftarrows$ **10** might be antarafacial to a greater extent than the minimum suggested by the difference between deuterium scrambling and racemization rate constants, k_{ds} and k_α.

And it raised the question: what mechanism is responsible for the epimerization?[42]

To examine the stereochemistry of the methylenecyclobutane isomerization in still greater detail, and to assure that deuterium scrambling and racemization processes should be measured under identical conditions, and be equally subject to secondary deuterium isotope effects, kinetic work on an optically active analog of **9** stereochemically labeled at migration origin, migration terminus, and migrating carbon was undertaken. The results obtained confirm the substantial antarafacial component inferred here, and provide other stereochemical information.[43]

Experimental Section

Gas-phase optical rotations were measured on a Cary-60 spectrometer made available through the cooperation of Professor John Schellman. Except where noted otherwise, preparative and analytical glpc work was done on β,β'-oxydipropionitrile columns at 50–80°.

Partial Resolution of (*Z*)-1-Ethylidene-2-methylcyclobutane. Sodium borohydride (51. 1mg. 1.35 mmol), (−)-α-pinene ($[\alpha]^{23}\text{D}$ −47.6°; 482 mg, 3.54 mmol), and 1.35 ml of diglyme were added to a small flask. The mixture was stirred under nitrogen throughout the reaction. The temperature was lowered to 0° and boron trifluoride etherate (251 mg, 1.77 mmol) in 4.05 ml of diglyme was added dropwise over a period of 10 min. After 4 hr, **13**[33] (340 mg, 3.54 mmol) was added, followed by 0.8 ml of diglyme. The white precipitate that had formed disappeared within 1 hr. The reaction mixture was allowed to stand overnight at 0°. It was then diluted with 25 ml of water and extracted with pentane (3 × 25 ml). The pentane layer was washed with water (3 × 25 ml), dried over magnesium sulfate, and filtered; the pentane was removed by distillation. A vacuum line transfer of the pot residue resulted in 2.2 ml of volatile material from which 97.5 mg (57%) of (−)-**13** was isolated by preparative glpc: $[\alpha]^{27}_{222\text{ nm}}$ −870° (gas phase).

1-Methylene-2-methylcyclobutane. Sodium hydride (4.83 g of a 57% suspension in mineral oil, 0.1146 mol) was washed with pentane (3 × 10 ml). Phosphonium salt **14** (40.9 g, 0.0995 mol) and dry dimethyl sulfoxide (250 ml) were added, all under a nitrogen atmosphere. The mixture was stirred at 30° until hydrogen evolution had ceased, then the temperature was raised to 45° for 1 hr. Formaldehyde produced from paraformaldehyde (9.0 g, 0.30 mol of CH_2O) by heating with a small flame was bubbled into the reaction mixture at such a rate that the temperature did not rise above 40°. The mixture was allowed to stir overnight. Water (250 ml) was added to the reaction mixture and solid material was filtered and washed with a small portion of pentane. The aqueous phase was extracted with pentane (3 × 80 ml); the pentane layers were combined, dried ($MgSO_4$), filtered, and concentrated by spinning band distillation. Vacuum transfer of the pot residue gave 5.15 g of a solution which was purified further by glpc on a 20% Carbowax 20M column to give 0.976 g (12%) of product: nmr ($CDCl_3$) δ 1.12 (3 H, d, J = 7 Hz), 1.56 (1 H, m), 2.10 (1 H, m), 2.59 (2 H, m), 2.98 (1 H, m), 4.68 (2 H, quintet, J = 2.2 Hz,); mass spectrum M^+ m/e 82.079 (calcd for C_6H_{10}, 82.078).

Characterization of the Products of Pyrolysis of 1-Methylene-2-methylcyclobutane. A 200-ml static reactor[33] was charged with 1-methylene-2-methylcyclobutane (20 Torr pressure). The material was allowed to react for 26 hr at 339° and retrieved by standard vacuum line techniques. Analysis by glpc showed two compounds. The compound with the shorter retention time (8 min) was identical with starting material. The compound with the longer retention time (13 min) proved to be ethylidenecyclobutane: nmr δ 1.47 (3 H, d, J = 6.7 Hz, of quintets, J = 1.8 Hz), 1.93 (2 H, m), 2.63 (4 H, m), 5.07 (1 H, m); mass spectrum M^+ m/e 82.078 (calcd for C_6H_{10}, 82.078).

Partial Resolution of 1-Methylene-2-methylcyclobutane. Sodium borohydride (0.165 g, 4.46 mmol), (−)-α-pinene ($[\alpha]^{23}\text{D}$ −47.6°; 1.62 g, 11.9 mmol), and diglyme (4.9 ml) were added to a small flask. The mixture was stirred under a nitrogen atmosphere, the temperature lowered to 0°, and boron trifluoride etherate (0.845 g, 5.95 mmol) in diglyme (13.5 ml) was added. After 6 hr at 0–10°, 1-methylene-2-methylcyclobutane (0.976 g, 11.9 mmol) was added, and the mixture was allowed to stand overnight at room temperature. Pentane (15 ml) and ice-water (80 ml) were added. The pentane layer was separated, washed with ice-water (2 × 80 ml), dried (4Å molecular sieves), vacuum transferred, and purified by preparative glpc to yield optically active 1-methylene-2-methylcyclobutane: 0.390 g, 80%, $[\alpha]^{27}_{220\text{ nm}}$ +193° (gas phase).

Kinetics of Racemization of (−)-(*Z*)-1-Ethylidene-2-methylcyclobutane. Samples of the partially resolved hydrocarbon (−)-**13** were introduced into a static reactor at about 10 Torr and kept at 332°

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[41] R. A. Alberty and W. G. Miller, *J. Chem. Phys.*, **26**, 1231 (1957).

[42] Compare C. Ullenius, P. W. Ford, and J. E. Baldwin, *J. Amer. Chem. Soc.*, **94**, 5910 (1972); M. Arai and R. J. Crawford, *Can. J. Chem.*, **50**, 2158 (1972).

[43] J. E. Baldwin and R. H. Fleming, *J. Amer. Chem. Soc.*, **95**, 5261 (1973).

for selected times. The product mixture was subjected to preparative glpc; the purified *Z* isomer thusly isolated was transferred to a gas cell and its rotation was measured. Then the sample was combined with a known amount of cyclohexene, and quantitative glpc analysis of the *Z* isomer plus cyclohexene mixture made possible calculation of the amount of (−)-**13** responsible for the observed rotation.

The specific rotations calculated depend on the assumption that equal molar quantities of cyclohexene and **13** cause equal peak areas using a thermoconductivity glpc detector. However, the kinetic determination is independent of this assumption, since first-order rate constants are independent of absolute values of concentration. The data are collected in Table I and delineated in Figure 1.

Kinetics of Rearrangement and Racemization of (+)-1-Methylene-2-methylcyclobutane. The optically active hydrocarbon (+)-**15** was introduced into the 300-ml static reactor at about 20 Torr at 333° and kept at this temperature for a set period. The thermolysis mixture was isolated and analyzed by glpc; this procedure gave the molar fraction of ethylidenecyclobutane produced. The (+)-**15** component was purified by preparative glpc, and its specific rotation was measured in the gas phase, using an improved technique described above. The data for these kinetic runs are collected in Table II and displayed in Figure 3.

Thermal Rearrangements of Methylenecyclobutanes. Degenerate Rearrangement of Optically Active 1-(*Z*)-(1-Deuterioethylidene)-2-methyl-*trans*-3,4,4-trideuteriocyclobutane[1]

John E. Baldwin* and Ronald H. Fleming[2]

Contribution from the Department of Chemistry, University of Oregon, Eugene, Oregon 97403.
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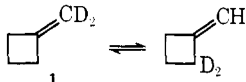
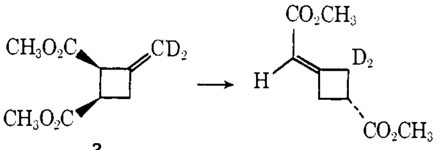
Abstract: 1-(*Z*)-(1-Deuterioethylidene)-2-methyl-*trans*-3,4,4-trideuteriocyclobutane at 332° isomerizes degenerately to give three other (*Z*)-1-ethylidene-2-methylcyclobutanes, one having the 3-deuterium label cis to the 2-methyl group, and the two cis–trans isomers of 1-ethylidene-2-methyl-2,3,4,4-tetradeuteriocyclobutane. The rate constants for these processes give a direct measure of the extent to which this methylenecyclobutane automerization by 1,3-carbon migration occurs with stereochemistry appropriate to an orbital symmetry allowed reaction: 77%. These three rate constants, together with the rate of racemization of (−)-(*Z*)-(1-deuterioethylidene)-2-methyl-*trans*-3,4,4-trideuteriocyclobutane and the assumption that stereochemistry at C(3) is preserved except possibly during 1,3-carbon shifts, lead to a quantitative estimate for the extent to which the 1,3-shift is antarafacial with respect to the allylic compondent: 65%.

The degenerate methylenecyclobutane rearrangement, which thermally equilibrates C(α), C(2), and C(4) methylene units (**1** ⇌ **2**),[3,4] has not been thoroughly studied.



1 2

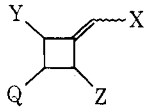
Prior to our work, only a single stereochemical result had been reported (but not published): the optically active diester **3** was rearranged to a product mixture from which the (−)-antipode **4** was isolated through resolution, then shown by nmr spectroscopy to have the deuterium label positioned as shown.[5]



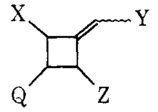
3 4

At least two factors partially responsible for the lack of stereochemical information on this 1,3-sigmatropic carbon migration may be surmised: the stereochemical problem, in an operational sense, was certain to be challenging, if not numbingly complicated; and the diradical mechanistic formalism proposed for the parent isomerization may have predisposed some to anticipate stereorandomized product mixtures from hydrocarbon substrates.

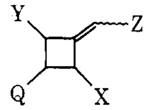
The potential complexity of labeled methylenecyclobutanes *is* awesome. Consider, by way of illustration, the labeled molecule **5**. Through 1,3-carbon migrations the analogs **6** and **7** could be reached. Each of these three gross structures could exist in 16 isomeric forms, and hence thermal equilibration of one starting material could in principal lead to an equilibrium mixture of 48 isomers (24 *dl* pairs)!



5



6



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Thermal isomerization of one isomer of **5** through a 1,3-carbon shift would leave one labeled center unchanged, and accordingly eight isomers of **6** and eight isomers of **7** could be formed directly at different rates. This enumeration extended to other possible starting

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[1] Supported by the National Science Foundation and Hoffmann-La Roche Inc.

[2] National Science Foundation Predoctoral Trainee, 1968–1972.

[3] J. P. Chesick, *J. Phys. Chem.*, **65**, 2170 (1961).

[4] W. von E. Doering and J. C. Gilbert, *Tetrahedron, Suppl.*, 7, 397 (1966).

[5] W. von E. Doering, Lecture, 21st National Organic Chemistry Symposium of the American Chemical Society, Salt Lake City, Utah, June 1969.