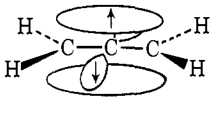
based on the conservation of symmetry of wave functions during reactions[19] on the grounds that chemical reactions rarely can, and never need to, involve the retention of symmetry during their intermediate phases. This, however, is a rather exceptional case. Orbital overlap will strongly tend to constrain the reacting carbon atom to approach ethylene in the plane bisecting the ethylenic HCH groups. Under these conditions, orbitals which are antisymmetric with respect to reflection in that plane will have very little tendency to mix with symmetric ones. There will therefore be a very high probability that the reaction of ^{1}S carbon with ethylene will yield **1** in the excited S_1 state.

Our MINDO/2 calculations predict the S_1 state of **1** to lie 15 kcal/mol above the S_0 state. It is also easily seen that this separation should decrease with an increase in the apical angle (*i.e.*, C$\ddot{C}$C) of **1**. Thus increasing this angle to 180° without rotation of the methylene groups would lead to a planar rotamer (**5**) of **2**. Here there are two NBMO's, *i.e.*, an AO of the central carbon atom and an allylic NBMO. The S_0 and S_1 states are then orbitally degenerate. There should therefore be a strong coupling between the $S_0 \rightarrow S_1$ electronic transition and the normal mode of vibration of the three-membered ring of **1** indicated in **6**. The electronic excitation in S_1 **1** should therefore be very much available for internal conversion to precisely the vibrational mode needed to transform **1** to **2**. This excitation energy is greater than our estimate of the activation energy required for this rearrangement. Furthermore, the ^{1}S state of carbon lies 33 kcal/mol above the ^{1}D state. The reaction with ethylene to form **1** will be correspondingly more exothermic. The excess energy will go into vibrational energy of **1** and, as has been previously pointed out,[6] a large part of this vibronic energy should again go into the normal mode of vibration indicated in **6**. It is therefore not at all surprising that the reaction of ^{1}S carbon atoms with olefins leads exclusively to allenes.[5]



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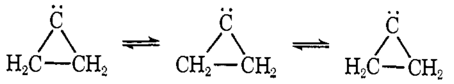

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On the other hand, the reaction of a ^{1}D carbon atom with ethylene is both less energetic and can, and should, lead to the lowest (S_0) singlet state of **1**. Here it is very likely that there will be initially insufficient vibrational energy in the normal mode of **6** for immediate conversion to **2**. In this case the excess vibronic energy will be lost, leaving **1** in its lowest singlet state (S_0). Our calculations then imply that rearrangement to cyclopropene (**4**) and reaction with ethylene to form spiropentane (**3**) should both occur more easily than rearrangement to allene (**2**). This of course is entirely consistent with the results reported by Skell and Engel.[5] The products from ^{1}D carbon atoms and olefins contain no allenes, consisting of a mixture of spiropentanes and unidentified products. If we are right in our prediction that rearrangement of **1** to **4** should be as facile as addition of **1** to olefin, complex products might be expected from secondary reactions of the resulting cyclopropenes.

(19) H. C. Longuet-Higgins and E. W. Abrahamson, *J. Amer. Chem. Soc.*, **87**, 2045 (1965); R. Hoffman and R. B. Woodward, *ibid.*, **87**, 2046 (1965).

Thermal Rearrangements of Methylenecyclobutanes. Kinetics of Equilibration of (*E*)- and (*Z*)-1-Ethylidene-2-methylcyclobutane and *cis*- and *trans*-1-Methylene-2,4-dimethylcyclobutane[1]

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

Contribution from the Department of Chemistry, University of Oregon, Eugene, Oregon 97403. *Received February 12, 1973*

Abstract: The isomeric methylenecyclobutane systems (*E*)- and (*Z*)-1-ethylidene-2-methylcyclobutane and *cis*- and *trans*-1-methylene-2,4-dimethylcyclobutane have been synthesized, identified, and thermally equilibrated at 332°. The two 1-(1-deuterioethylidene)-2-methylcyclobutanes have been prepared and equilibrated with the corresponding 1-ethylidene-2-deuterio-2-methylcyclobutanes. The rate constants obtained reveal some striking stereochemical effects. The 1-methylene-2,4-dimethylcyclobutanes rearrange preferentially to the *E* isomer of 1-ethylidene-2-methylcyclobutane. The *Z* isomer of 1-ethylidene-2-methylcyclobutane isomerizes with predominant cleavage of the more substituted C(2)–C(3) bond, but the *E* isomer does the opposite—the C(3)–C(4) bond is preferentially broken. Both *E* and *Z* isomers show net retention of geometrical configuration about the ethylidene unit during 1,3-carbon migration originating from C(2).

Kinetic studies on the gas phase unimolecular cycloreversion of methylenecyclobutane (**1**) to ethylene and allene[3-6] and on the conversion of spiropentane (**2**) to both methylenecyclobutane and the ethylene–allene

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(1) Supported by the National Science Foundation and Hoffmann-La Roche Inc.

(2) National Science Foundation Predoctoral Trainee, 1968-1972.

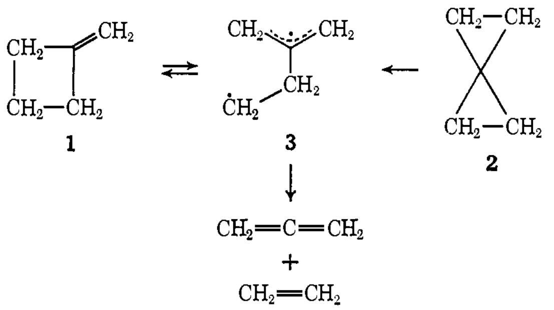
(3) P. J. Burkhardt, Dissertation, University of Oregon, 1962.

(4) J. P. Chesick, *J. Phys. Chem.*, **65**, 2170 (1961).

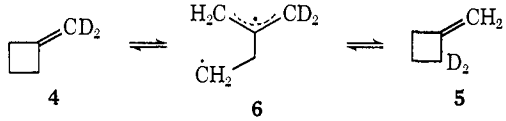
(5) R. L. Brandaur, B. Short, and S. M. E. Kellner, *ibid.*, **65**, 2269 (1961).

(6) W. J. Engelbrecht and M. J. DeVries, *J. S. Afr. Chem. Inst.*, **23**, 163, 172 (1970).

pair[3,7] led to postulation of reaction through a 2-(dimethylene)allylene diradical intermediate (**3**).[4]



Chesick[4] recognized that a suitably labeled analog of methylenecyclobutane might exhibit a degenerate rearrangement, or automerization.[8] The proposal was soon demonstrated valid through the synthesis and pyrolysis of dideuteriomethylenecyclobutane (**4**);[9] at 287–355° in the gas phase, compound **4** was equilibrated with 1-methylene-2,2-dideuteriocyclobutane (**5**) with activation parameters E_a = 49.5 kcal/mol and log A = 14.8.



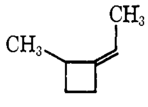
Doering and Gilbert[9] assumed that an intermediate **6** was involved, and estimated an energy barrier of 4.2 kcal/mol between intermediate and transition state for methylenecyclobutane formation. Transition-state geometries appropriate to concerted pathways were judged likely to have exorbitantly high energies as a result of poor orbital overlap and unfavorable steric interactions.

This automerization may now be classed as a 1,3-sigmatropic carbon migration,[10,11] a type of rearrangement still inadequately understood. While many examples are known, both in hydrocarbons and in systems substituted with highly polar functionality, kinetic and stereochemical results have been mechanistically indecisive.

Some examples have been rationalized in terms of diradical intermediates, to account for product distributions showing stereorandomness or low stereoselectivity. Others have given products consistent with the stereochemical predictions of orbital symmetry theory (inversion at carbon and suprafacial migration across one side of the allylic unit), products the diradical theory and least-motion accretions cannot be stretched to explain.

In part because of our concern with the methylenecyclobutane rearrangement and with allene–olefin cycloadditions,[12] and in part because of our belief that some more general mechanistic theory, something beyond the rigid categories of diradical-nonconcerted and symmetry allowed-concerted,[13] must be gained before the stereoselectivities of 1,3-sigmatropic rearrangements can be predicted with fair accuracy, we have undertaken a study of some methyl- and deuterium-labeled analogs of the methylenecyclobutane system.

Here we report on the thermal equilibrations of isomers **7**–**10**, and on the automerizations **7**-*α*-*d* ⇄ **7**-*2*-*d* and **8**-*α*-*d* ⇄ **8**-*2*-*d*.



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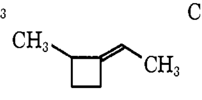

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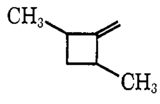

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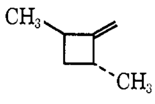

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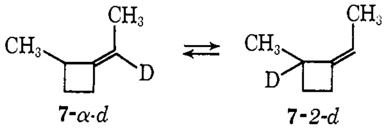
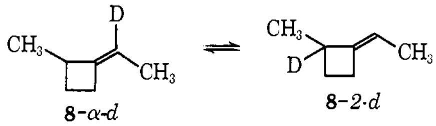


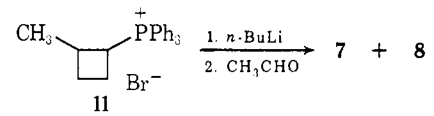


In other manuscripts, evidence is presented revealing a substantial component of antarafacial allylic utilization during the 1,3-carbon migration,[14] a thermal epimerization at C(2) at rates competitive with carbon migration,[15] and the ratio between carbon migration products having stereochemistry corresponding to symmetry allowed and symmetry forbidden processes.[15]

Results

A mixture of the two 1-ethylidene-2-methylcyclobutanes **7** and **8** was synthesized by an extension of the method of Bestmann and Kranz.[16] Reaction of 1,3-dibromobutane with 2 equiv of methylenetriphenylphosphorane in tetrahydrofuran gave the cyclobutylphosphonium salt **11**, separable from methyltriphenylphosphonium bromide by recrystallization from water. Generation of 2-methylcyclobutylidenetriphenylphosphorane with *n*-butyllithium, and Wittig condensation with acetaldehyde, completed the sequence.

$$BrCH_2CH_2CHBrCH_3 + 2CH_2{=}PPh_3 \longrightarrow$$



The isomeric products were separated by preparative glpc and characterized spectroscopically. Distinguishing which isomer had which configuration was a subtle task, accomplished utilizing three supportive types of evidence.

First, proton nmr chemical shift differences: the isomer having the C(2) methyl resonance most downfield, at δ 1.19, was assigned the *Z* configuration (**7**). In the *E* isomer (**8**), the corresponding signal fell at δ 1.07.

Several analogies for these assignments may be cited. In the 3-methyl-2-pentenes the C(5) methyl resonance

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(7) M. C. Flowers and H. M. Frey, *J. Chem. Soc.*, 5550 (1961).

(8) A. T. Balaban and D. Farcasiu, *J. Amer. Chem. Soc.*, **89**, 1958 (1967).

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

(10) R. B. Woodward and R. Hoffmann, *J. Amer. Chem. Soc.*, **87**, 2511 (1965).

(11) R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, 8, 781 (1969).

(12) J. E. Baldwin and R. H. Fleming, *Fortschr. Chem. Forsch.*, **15**, 281 (1970).

(13) J. E. Baldwin, A. H. Andrist, and R. K. Pinschmidt, Jr., *Accounts Chem. Res.*, 5, 402 (1972).

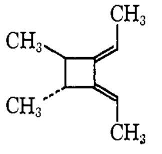
(14) J. E. Baldwin and R. H. Fleming, *J. Amer. Chem. Soc.*, **94**, 2140 (1972).

(15) J. E. Baldwin and R. H. Fleming, *ibid.*, **95**, 5256, 5261 (1973).

(16) H. J. Bestmann and E. Kranz, *Chem. Ber.*, **102**, 1802 (1969).

comes at δ 0.97 in the Z isomer, and at δ 0.95 for the E form. In the 3,4-dimethyl-2-pentenes, the methyl protons of the isopropyl moiety are observed at δ 0.98 and 0.94 for the Z and E isomers, respectively.[17,18]

Stereochemically more constrained pairs of compounds containing the 1-ethylidene-2-methylcyclobutyl unit exhibit the same regularity. The C(2,3) methyl resonances for the isomers **12** and **13** are at δ 1.18 and 1.08.[19]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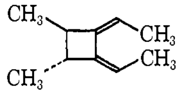
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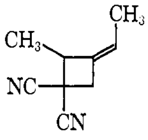
Compounds **14** and **15** similarly show a significant difference in chemical shift between the C(2) methyl resonances: they come at δ 1.53 and 1.42.[20]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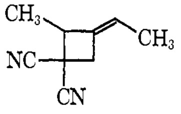
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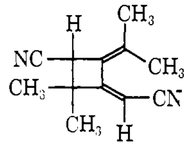
Thus, the chemical shifts of C(2) methyl protons in compounds **7** and **8** conform with a general pattern: the more sterically crowded Z isomer in each pair has this signal more downfield.

Second, the ^5J coupling constants between the allylic ring protons and methyl protons of the ethylidene group in **7** and **8** supported the same configurational assignment. In **7**, $J_{2,\beta} = 1.5$ and $J_{4,\beta} = 2.0$ Hz. In the E isomer **8**, $J_{2,\beta} = 2.1$ and $J_{4,\beta} = 1.5$.

Transoid homoallylic coupling constants are typically somewhat larger than cisoid couplings.[21] Differences of 0.3–0.4 Hz are common. In the 1,2-dimethylenecyclobutane derivative **16** the difference was a surprisingly large 1.2 Hz.[22]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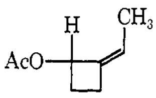
Kelsey and Bergman[23] made tentative configurational assignments for compounds **17** and **18** as shown; the vinylic methyl of the first had cisoid $J_{2,\beta} = 1.0$ Hz, while the second had transoid $J_{2,\beta} = 1.5$ Hz. Spin–spin coupling between C(4) and C(β) protons was not reported.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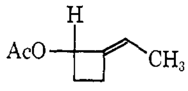
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Thus, the greater absolute magnitude of transoid relative to cisoid $^5J_{HH}$ homoallylic couplings both in acyclic and in ethylidenecyclobutyl systems seems general, and the structural assignments **7** and **8** are consistent with the pattern.

Third, the ^{13}C nmr spectra of isomers **7** and **8**, summarized in Table I, led to the same stereochemical assignment. The shielding nature of the vinylic methyl group can be seen in the chemical shifts of the C(2) carbon atoms in **7** and **8**, and again in those for the C(4) allylic methylene carbons. Thus, the resonance for the methine carbon C(2) appears further downfield in the E isomer (**8**) than in the Z isomer (**7**), and the resonance for the C(4) allylic methylene carbon comes further upfield in **8** than in **7**. Gajewski used the analogous spectral characteristics of **14** and **15** in assigning their structures,[20] and Cheney and Grant[24] have provided a theoretical discussion of the phenomenon.

Table I. Carbon Magnetic Resonance Spectra of (E)- and (Z)-1-Ethylidene-2-methylcyclobutane

Compd	Chemical shift[a] (ppm)	Multiplicity	Assignment
7	46.0	s	C-1
	76.0	d	C-α
	153.5	d	C-2
	163.2	t	C-4
	165.7	t	C-3
	171.1	q	C-β
	178.3	q	C-2 methyl
8	44.5	s	C-1
	78.5	d	C-α
	152.3	d	C-2
	164.5	t	C-3 or C-4
	165.0	t	C-3 or C-4
	171.7	q	C-β
	178.5	q	C-2 methyl

[a] Relative to CS$_2$. The spectrometer was locked on the deuterium resonance of the solvent acetone-d_6; the chemical shift of the external standard, iodomethane in acetone-d_6, was taken as 214 ppm upfield from carbon disulfide.

Pyrolyses of the 1-ethylidene-2-methylcyclobutanes at 320° gave two new compounds, identified as the isomeric *cis*- and *trans*-2,4-dimethyl-1-methylenecyclobutanes **9** and **10**.

Stereochemical assignments for the two new hydrocarbons were made through examination of nmr spectral parameters and consideration of symmetry requirements. Because the trans isomer has a C_2 symmetry axis, it contains no unique hydrogen. In the cis isomer, however, both C(3) hydrogens cut by the symmetry plane are distinct and separate. The nmr spectrum of the isomer assigned as **10** showed the C(3) protons as a two-hydrogen triplet, while the other, **9**, had a multiplet which integrated for one C(3) hydrogen; the other C(3) proton resonance was obscured by methyl signals.

To confirm these stereochemical designations, both

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(17) Chemical shifts were taken from "Selected NMR Spectral Data," American Petroleum Institute Research Project 44, Carnegie Press, Pittsburgh, Pa., Serial No. 377, 378, 403, and 404.

(18) Account has been taken of the subsequent revision of the configurational assignment: F. H. A. Rummens, *Recl. Trav. Chim. Pays-Bas*, 84, 1003 (1965).

(19) J. J. Gajewski and W. A. Black, *Tetrahedron Lett.*, 899 (1970).

(20) J. J. Gajewski and L. T. Burka, *J. Amer. Chem. Soc.*, 93, 4952 (1971).

(21) W. Brügel, "Nuclear Magnetic Resonance Spectra and Chemical Structure," Vol. 1, Academic Press, New York, N. Y., 1967, p 48.

(22) G. R. Hansen, K. W. Ratts, and J. T. Marvel, *Chem. Commun.*, 918 (1970).

(23) D. R. Kelsey and R. G. Bergman, *J. Amer. Chem. Soc.*, 93, 1941 (1971).

(24) B. V. Cheney and D. M. Grant, *ibid.*, 89, 5319 (1967).

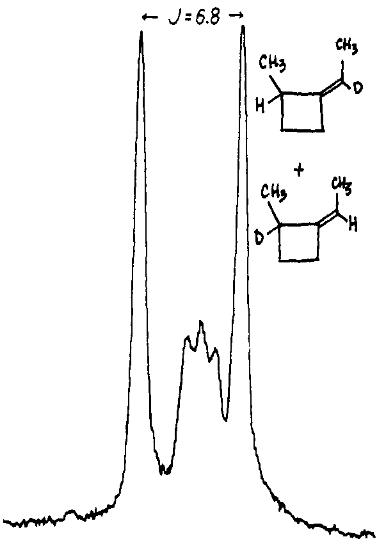
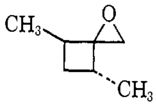


Figure 1. The C(2)–CH_3 region of the nmr spectrum of 7-*α-d* and 7-*2-d*, from pyrolysis of 7-*α-d* for 17.2 × 10^3 sec at 332°.

olefins were converted to the corresponding epoxide(s) by treatment with *m*-chloroperbenzoic acid in pentane. The trans olefin **10** can give but a single, asymmetric epoxide. The cis compound **9** can give two epoxides, each having a plane of symmetry relating the methyl protons. The isomer of shorter glpc retention time, the trans compound according to the nmr spectroscopic argument, gave as expected one epoxidation product (**19**) with two methyl doublets (J = 7.5 Hz) centered at δ 1.03 and 1.17. The second isomer, thought to be the cis olefin, gave a mixture of two epoxides (**20** and **21**) each having a single six-hydrogen methyl doublet.



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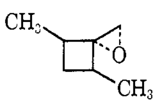

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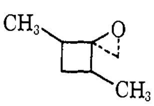

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Thus the stereochemical assignments were conclusively corroborated.

Samples of the 1-ethylidene-2-methylcyclobutanes labeled with deuterium at C(α) were prepared by condensing 2-methylcyclobutylidenetriphenylphosphorane with deuterioacetaldehyde. Three base-catalyzed exchanges between nitroethane and deuterium oxide, then a Nef reaction, gave the labeled acetaldehyde required.[25]

The exchange reaction was most easily effected by heating equal volumes of deuterium oxide and nitroethane with a larger than recommended[25] amount of catalyst for 3 days. Recrystallized **11** was used to minimize the amount of deuterioacetaldehyde required; otherwise the reaction conditions used for the unlabeled compounds were unmodified.

Rates of thermal isomerizations were measured using a 300-ml glass reaction vessel and an aluminum heating block having a close-fitting spherical cavity. Samples were introduced into the vessel and removed using standard vacuum line techniques, then trapped with liquid nitrogen in a small section of the vacuum line. This section was equipped with a serum cap through which samples could be removed by syringe and analyzed by glpc. Product ratios starting from **7** and from **8** as a function of time are given in Tables II and III.

Table II. Product Ratios from the Pyrolysis of (*Z*)-1-Ethylidene-2-methylcyclobutane (**7**) at 332°

Time (10^3 sec)	**7**	**8**	**9**	**10**	Unknown products
0	0.962	0.038			
4.80	0.923	0.058	0.002	0.007	0.009
9.06	0.898	0.072	0.006	0.012	0.012
12.5	0.896	0.073	0.006	0.015	0.011
22.1	0.828	0.114	0.020	0.028	0.011
32.5	0.782	0.139	0.030	0.037	0.012
43.2	0.725	0.179	0.043	0.044	0.010

Table III. Product Ratios from the Pyrolysis of (*E*)-1-Ethylidene-2-methylcyclobutane (**8**) at 332°

Time (10^3 sec)	**7**	**8**	**9**	**10**	Unknown products
0	0.031	0.969			
7.31	0.053	0.809	0.076	0.049	0.013
15.5	0.077	0.707	0.122	0.082	0.012
23.2	0.092	0.641	0.150	0.100	0.017
29.2	0.101	0.628	0.150	0.107	0.013
41.0	0.123	0.571	0.169	0.118	0.020

Nmr analysis was used to determine the rate of deuterium scrambling of racemic 7-*α-d* at 332° to give an equilibrium mixture of 7-*α-d* and 7-*2-d*. The deuterated substrate was pyrolyzed for a selected interval of time, isolated from the four-component mixture by preparative glpc, then submitted to scrutiny by nmr spectroscopy. A C(2) methyl doublet (J = 6.8 Hz) was expected for those molecules (7-*α-d*) with hydrogen at C(2), and a triplet (J = 1.0 Hz) for those (7-*2-d*) with deuterium at C(2). Figure 1 shows an example of the ring methyl region of the nmr spectrum given by a mixture of 7-*α-d* and 7-*2-d* produced by pyrolysis of 7-*α-d* for 17.2 × 10^3 sec.

Pyrolysis of the *E* isomer 8-*α-d* was carried out in the same manner. The data are recorded in Tables IV and V. The equilibration of the four C_7H_{12} isomers was

Table IV. Kinetic Data for Deuterium Scrambling of 7-*α-d* at 332°

Reaction time (10^3 × sec)	Mole fraction 7-*2-d*	Mole fraction 7-*α-D*
0	0.0	1.0
8.10	0.23	0.77
17.2	0.37	0.63
25.4	0.44	0.56

Table V. Kinetic Data for Deuterium Scrambling of 8-*α-d* at 332°

Reaction time (10^3 × sec)	Mole fraction 8-*2-d*	Mole fraction 8-*α-d*
0	0.0	1.0
25.4	0.13	0.87
29.1	0.17	0.83
47.8	0.29	0.71
48.5	0.31	0.69
72.1	0.42	0.58

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(25) A. Murray and D. L. Williams, "Organic Synthesis with Isotopes," Vol. 2, Interscience, New York, N. Y., 1958, p 1359–1360.

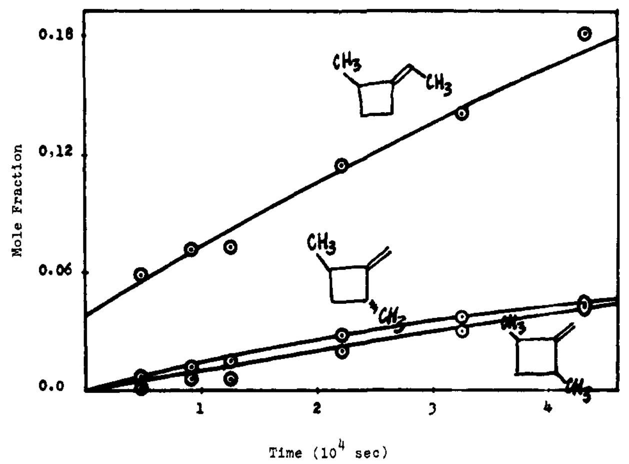

Figure 2. Experimental points and calculated lines for the concentrations of hydrocarbons **8**–**10** from the pyrolysis of **7** at 332°.

treated in terms of the general first-order reaction scheme shown.

$$\begin{tikzcd}
7 \arrow[r, shift left] \arrow[d, shift left] \arrow[dr, shift left] & 8 \arrow[l, shift left] \arrow[d, shift left] \arrow[dl, shift left] \\
9 \arrow[u, shift left] \arrow[ur, shift left] & 10 \arrow[u, shift left] \arrow[ul, shift left]
\end{tikzcd}$$

The rate constants found to give the lowest total sum of squared deviations between calculated and observed concentrations are presented in Table VI.

Table VI. First-Order Rate Constants for Thermal Equilibration of Isomers **7**–**10**

Reaction	$k \times 10^5$ sec^{-1}	Reaction	$k \times 10^5$ sec^{-1}
7 → **8**	0.48	**8** → **10**	0.89
7 → **9**	0.05	**9** → **7**	0.34
7 → **10**	0.13	**9** → **8**	4.2
8 → **7**	0.31	**10** → **7**	0.32
8 → **9**	1.37	**10** → **8**	3.8

The concentration of hydrocarbons produced through pyrolysis of **7** and of **8**, as calculated from the rate constants of Table VI, are shown with the experimentally determined values in Figures 2 and 3.

The rate constants for direct equilibration of *cis*- and *trans*-1-methylene-2,4-dimethylcyclobutane could not be established reliably through these kinetic studies. The time-dependent concentrations of the four compounds **7**–**10** are not very sensitive to changes in the rate constants for interconversion of the secondary products. This limitation is reflected in the calculations: the sum of the squared deviations of experimental and calculated concentrations was less sensitive to equal changes of $k(\mathbf{9} \rightarrow \mathbf{10})$ and $k(\mathbf{10} \rightarrow \mathbf{9})$ than to changes in any other k values. Thus, further kinetic work starting from **9** or **10** would have been necessary to gain reliable estimates for these two rate constants. The rate constants in Table VI were the best fit when $k(\mathbf{9} \rightarrow \mathbf{10}) = k(\mathbf{10} \rightarrow \mathbf{9}) = 0$; other studies indicate that they are probably not negligibly small.[15]

The deuterium scrambling data from Tables IV and V were first treated according to theory appropriate to a simple first-order approach to equilibrium. From the plots obtained (Figure 4), it was apparent that the approximation was satisfactory for the automerization of the *Z* isomer **7**, but not for automerization of the *E* compounds **8**-α-*d* ⇄ **8**-*2*-*d*.

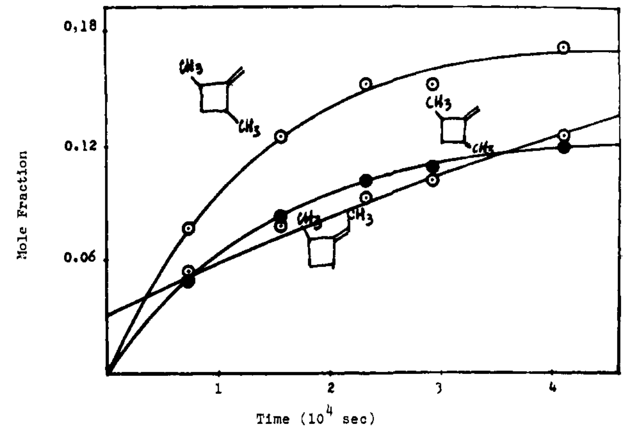

Figure 3. Experimental points and calculated lines for the concentrations of hydrocarbons **7**, **9**, and **10** from the pyrolysis of **8** at 332°.

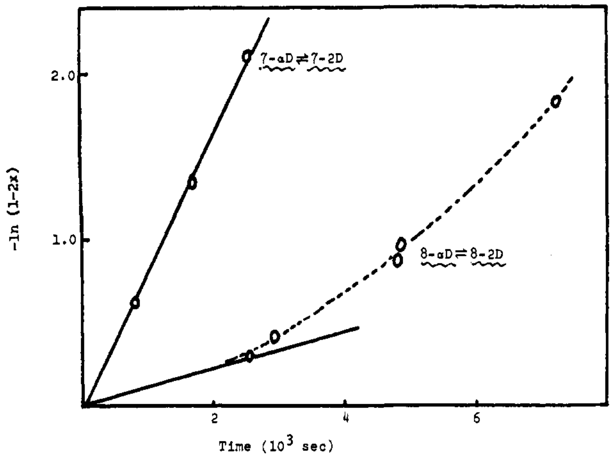

Figure 4. Kinetic plots for deuterium scrambling **7**-α-*d* ⇄ **7**-*2*-*d* and **8**-α-*d* ⇄ **8**-*2*-*d*.

Assuming that there is no significant equilibrium isotope effect for the **7**-α-*d* ⇄ **7**-*2*-*d* interconversion, for there is none in the **4** ⇄ **5** case,[9] one may calculate a 95% confidence interval[26] for the rate of deuterium scrambling, $k_{\mathrm{ds}} = k(\mathbf{7}\text{-}\alpha\text{-}d \rightarrow \mathbf{7}\text{-}2\text{-}d) + k(\mathbf{7}\text{-}2\text{-}d \rightarrow \mathbf{7}\text{-}\alpha\text{-}d) = 8.15 \pm 0.60 \times 10^{-5}\ \mathrm{sec}^{-1}$.

From the first two data points in Table V one may calculate an upper limit of 0.6×10^{-5} sec^{-1} for the direct reaction **8**-α-*d* → **8**-*2*-*d*. The equilibration of **8**-α-*d* with **8**-*2*-*d* is more efficiently accomplished indirectly, through the 1-methylene-2-deuterio-2,4-dimethylcyclobutanes.

Discussion

The 1-methylene-2,4-dimethylcyclobutanes **9** and **10** both rearrange preferentially to the *E* isomer **8** rather than to the *Z* isomer **7**, by a factor of about 12. At 332°, assuming equal preexponential factors, this corresponds to $\Delta E_a = 3.0$ kcal/mol.

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[26] T. Yamane, "Statistics: An Introductory Analysis," Harper and Row, New York, N. Y., 1967, p 418.

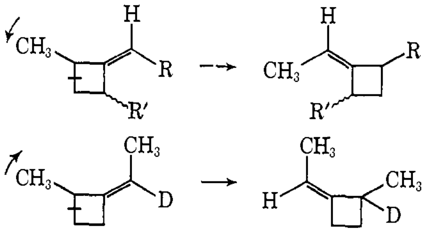
The Z isomer **7** rearranges with cleavage of the C(2)–C(3) bond more readily than by breaking the C(3)–C(4) bond; the ratio of rate constants (k(**7** → **8**) + k(**7**-α-d → **7**-2-d))/(k(**7** → **9**) + k(**7** → **10**)) is 25:1.

From the E isomer this ordering is reversed: the ratio of rate constants (k(**8** → **7**) + k(**8**-α-d → **8**-2-d))/(k(**8** → **9**) + k(**8** → **10**)) is 0.40:1!

The labeled Z isomer **7**-α-d, when it rearranges with C(2) as the migration origin, gives the deuterium scrambled Z isomer **7**-2-d preferentially over the E isomer **8** by a factor of 8.5 (ΔE_a = 2.6 kcal/mol). The labeled E substrate **8**-α-d shows a slighter preference for maintaining configuration during 1,3 migrations from C(2); the rate ratio k(**8**-α-d → **8**-2-d)/k(**8** → **7**) is 1.9:1 (ΔE_a = 0.8).

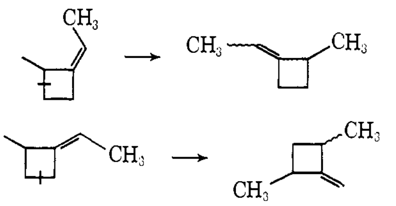
These three types of rate comparisons are all based on the partitioning of a single reactant, and differences in ground-state energies are not at issue.

Taken together, they may be generalized as follows. When C(2) is the migration origin, a methyl C(2) substituent prefers to rotate away from a syn-disposed C(α) proton, but toward a syn-positioned C(α) methyl.



R = H, R' = CH$_3$
R = CH$_3$, R' = H

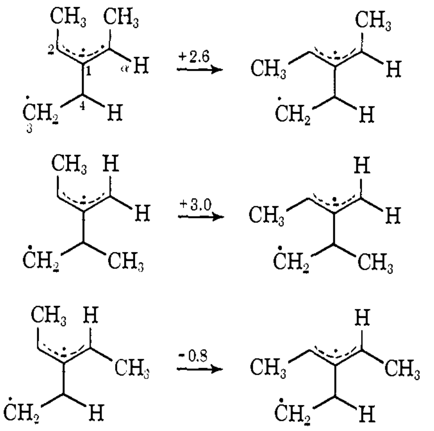
1,3-Sigmatropic carbon migrations in 1-ethylidenecyclobutane systems occur preferentially with the ring carbon syn to C(α) methyl as migration origin.



The diradical model applied to the parent methylenecyclobutane system involves full allylic resonance at the transition state.[27] The corresponding diradical models for the activated complexes of concern here may be listed, together with relative energies or relative heats of formation, by taking ΔE_a from reaction rate comparisons as directly reflected in ΔH_f magnitudes for the hypothetical diradicals.

Such an exercise leads to baffling inferences. The comparable ΔH_f changes for the two isomerizations shown below suggest, when considered in light of the diradical hypothesis, that 1,3-diaxial-like interactions in the allylic moiety and interactions between methyl substituents at C(2) and C(4) are not very significant. If they were, the first isomerization would be much less endothermic than the second.

Another comparison of roughly analogous type, however, is estimated to be exothermic! Schemes involving additive steric perturbations cannot account for these variations in a consistent and plausible manner.



These ΔH_f values could be modified by introducing widely different reversion-to-starting-material *vs.* 1,3-migration-completion rate ratios. But the simple diradical formalism the ΔH_f changes are based on cannot be sufficient. The inferences cannot be accepted as reasonable.

The principal mechanistic alternative, concerted reaction modes, might exhibit appropriate stereochemical preferences. These were sought through more detailed investigations with deuterium labeled and optically active substrates.[14,15]

Experimental Section

Proton nmr spectra were measured on Varian Associates HA-100 or XL-100-FT spectrometers. Carbon nmr spectra were measured using the XL-100-FT and a Varian Associates 620i computer. Deuterium exchange experiments were followed on Varian Associates A-60 or T-60 spectrometers. Infrared absorption spectra were run on a Perkin-Elmer Model 700 spectrophotometer, and mass spectra were run by Mrs. Mary Mitchell or Dr. Susan Rottschaefer on a CEC 110-21B instrument. Melting points were determined on a Kofler hot stage and are uncorrected.

A Perkin-Elmer F-11 chromatograph was used for some of the analytical glpc work, employing column A, 13 m × 0.5 mm open tubular column coated with DC-200/500, at 102°. The preparative and some analytical glpc work was done on a Varian Aerograph A-90-P3 instrument using column B, 5 m × 6 mm or 6 m × 6 mm 20% β,β'-oxydipropionitrile on 60–80 Chromosorb P, at 50–80°; or column C, 2.7 m × 9 mm 20% SE-30 on Chromosorb W, at 120–130°.

2-Methylcyclobutyltriphenylphosphonium Bromide (11).[16] To 8.1 g (0.338 mol) of sodium hydride suspended in 600 ml of tetrahydrofuran, 100 g (0.280 mol) of methyltriphenylphosphonium bromide and one drop of absolute ethanol were added. The mixture was stirred and heated to 50–54° for 8 hr in a nitrogen atmosphere. The mixture was allowed to cool and the clear yellow solution was forced with nitrogen pressure through a glass tube into another flask, care being taken not to transfer any of the precipitated sodium bromide. To this solution, 30.8 g (0.142 mol) of 1,3-dibromobutane was added and the mixture was stirred and heated to 50° for 9 hr. The white precipitate of **11** and by-products was filtered, recrystallized from 100 ml of water, and dried: 20 g (35%), mp 245–250° (lit.[16] mp 246–248°); second crop, after a second recrystallization: 6.5 g, mp 220–252°.

1-Ethylidene-2-methylcyclobutane (7 and 8). A mixture of 2-methylcyclobutyltriphenylphosphonium bromide in tetrahydrofuran was prepared as described above, using 17 g (0.707 mol) of sodium hydride, 210 g (0.588 mol) of methyltriphenylphosphonium bromide, 1.5 l of tetrahydrofuran, and 64.8 g (0.300 mol) of 1,3-dibromobutane. This salt mixture was treated with 366 ml of 1.61 *M* (0.588 mol) *n*-butyllithium, stirred for 0.5 hr, and cooled to 0°. To the thus formed deep red solution, 34.4 ml (0.618 mol) of freshly distilled acetaldehyde was added and the mixture was stirred for 1.5 hr. All of the above operations were carried out under a nitrogen atmosphere. The resulting mixture was filtered and 1.0 l. of pentane was added to the filtrate. This solution was washed with ice-water (20 × 100 ml). A white precipitate appeared in the organic layer after six extractions. It was removed by filtration.

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[27] S. W. Benson and H. E. O'Neal, "Kinetic Data on Gas Phase Uni-Molecular Reactions," NSRDS-NBS 21, U. S. Government Printing Office, Washington, D.C., 1970, p 18.

The resulting tetrahydrofuran-free pentane solution was dried over magnesium sulfate and the pentane and hexane (from the *n*-butyllithium solution) were removed by distillation. A small amount of xylene was added as chaser and the product was quickly distilled, bp 94–130°. The distillate was fractionated on a Teflon angular distillation apparatus. Fractions rich in **7** and **8** had bp 98–99.5°. A total of six fractions contained approximately 13.0 g (46.0%). Although little fractionation of the two isomers occurred, they could be separated preparatively by glpc (column B): their relative retention times were 0.92 and 1.00.

The nmr spectrum of the *Z* isomer **7** showed a doublet at δ 1.19 (3 H, J = 6.8 Hz, C-2-CH$_3$) and a multiplet at 1.49 (3 H, C-α-CH$_3$) in which the following coupling constants could be distinguished: 6.5 (to C-α-H), 1.5 (to C-2-H), and 2.0 Hz (to C-4-H$_2$). Other signals occurred at δ 2.06 (m, 1 H), 2.50 (m, 2 H), 2.98 (m, 1 H), and 5.01 (q of q, 1 H, J = 6.8 and 2.3 Hz). A 1-H multiplet was obscured by the signal at δ 1.49. The gas-phase infrared spectrum showed bands at 2980, 1460, 1450, 1380, 1080, 940, 810 cm^{-1}. The mass spectrum showed a molecular ion at *m/e* 96 and major fragment ions at *m/e* 81, 68, 67, 54, 53, 41, and 39.

The *E* isomer **8** had a doublet at δ 1.07 (3 H, J = 6.8 Hz, C-2-CH$_3$) and a multiplet at 1.47 (3 H, C-α-CH$_3$) in which the following couplings could be distinguished: 6.7 (to C-α-H), 2.1 (to C-2-H), and 1.5 Hz (to C-4-H$_2$). There was a complex multiplet at 2.06 (1 H), another at 2.51 (2 H), another at 2.88 (1 H), and a symmetrical multiplet at 5.05 ppm (1 H). A 1-H multiplet was obscured by the signal at δ 1.47. The gas-phase infrared spectrum showed peaks at 3060, 2980, 1460, 1450, 1370, 1320, 1080, 1020, 975, and 810 cm^{-1}, and the mass spectrum showed a molecular ion at *m/e* 96 and major fragment ions at *m/e* 81, 68, 67, 54, 53, 41, and 39.

Products of Pyrolysis of 1-Ethylidene-2-methylcyclobutane. Pyrolysis of either **7** or **8** gave starting material plus three other products. Several runs were made. In a typical run, about 100 μl of **7** was placed in a 35-ml Carrius tube. The sample was degassed, the tube was sealed, and the compound was pyrolyzed at 320° for 48 hr. The 99-μl product mixture obtained was analyzed by glpc (column B); the data are summarized in Table VII. Two other products of less than 1% glpc peak area were also detected.

Table VII. Retention Time and Peak Area Glpc Data for Products from Pyrolysis of **7**[a]

Product	Rel retention time	Rel peak area (%)
10 (trans)	0.615	11.4
9 (cis)	0.667	14.0
8 (*E*)	0.928	45.2
7 (*Z*)	1.000	29.4

[a] 320°, 48 hr.

The nmr spectrum of cis isomer **9** showed a doublet methyl resonance pattern at δ 1.09 on top of a single proton multiplet (7 H total rel intensity), a broadened quartet, J = 9 Hz, at δ 2.26 (1 H), a broad multiplet at δ 2.73 (2 H), and a triplet at δ 4.65 (2 H). The gas-phase infrared spectrum showed prominent absorption at 3090, 2950, 2890, 1670, 1460, 1380, and 870 cm^{-1}. Mass spectrum: molecular ion at *m/e* 96. Major fragment ions at *m/e* 81, 68, 67, 54, 53, 44, 41, and 39.

The nmr spectrum of trans isomer **10** showed a doublet, J = 7 Hz, at δ 1.15 (6 H), triplet J = 7.5 Hz, at δ 1.71 (2 H), broad multiplet at δ 2.97 (2 H), and a triplet, J = 2.4 Hz, at δ 4.76 (2 H). Double irradiation at δ 2.97 collapsed the other three signals to singlets. The gas-phase infrared spectrum showed bands at 3080, 2980, 2890, 1670, 1460, 1380, and 875 cm^{-1}; mass spectrum molecular ion *m/e* 96, major fragment ions, *m/e* 81, 68, 67, 54, 53, 41, 39.

Epoxidation Products from *cis*-1-Methylene-2,4-dimethylcyclobutane (9). *cis*-1-Methylene-2,4-dimethylcyclobutane (about 9 mg), *m*-chloroperbenzoic acid (60 mg), and 2.5 ml of pentane were stirred at room temperature for 8 hr. Volatile materials were removed from the reaction mixture by a vacuum transfer. Glpc of the volatile material showed two products (retention times of 5.3 and 6.0 min on column A) in a ratio of 53:47. The two products were collected by preparative glpc (column C, 120°). Nmr data are given in Table VIII. The mass spectrum of the isomer of shorter retention time showed a molecular ion at *m/e* 112 and major fragment ions at *m/e* 97, 83, 70, 69, 67, 56, 55, 44, 42, 41, and 39; the isomer of longer retention time showed a molecular ion at *m/e* 112 and major fragment ions at *m/e* 97, 83, 71, 56, 55, 44, 42, 41 and 39.

Table VIII. Nmr Data for Epoxides **19–21**

Signal assignment	Chemical shift, multiplicity, coupling constant (Hz) **19**	**20** or **21**[a,b]	**20** or **21**[a]
CH$_3$-C-2,4	δ 1.03, d, 7.5 1.17, d, 7.5	1.01, d, 7.5	1.00, d, 7.5
H$_2$C-α	2.62, 2.87, AB pattern, J_{AB} = 5	2.68, s	2.76, s
H-C-2,4 and H$_2$-C-3	2.5–3.1, m 0.9–1.95, m	2.78, m 1.29, m 2.38, m	2.66, m 1.20, m 2.28, m

[a] No attempt is made to distinguish whether the methyl groups are cis or trans to the epoxide oxygen. [b] Isomer of shorter retention time.

Epoxidation Product from *trans*-1-Methylene-2,4-dimethylcyclobutane (10). *trans*-1-Methylene-2,4-dimethylcyclobutane (about 7 mg), *m*-chloroperbenzoic acid (60 mg), and 2.5 ml of pentane were stirred at room temperature for 8 hr. Volatile materials were removed from the reaction mixture by a vacuum transfer. Glpc of the volatile material showed one product (retention time of 5.7 min on column A) which was collected on glpc column C at 130°. Nmr data are given in Table VIII. The mass spectrum showed a molecular ion at *m/e* 112 and major fragment ions at *m/e* 97, 83, 71, 69, 56, 55, 44, 42, 41, and 39.

Nitroethane-*1,1-d*$_2$.[25] A mixture of equal volumes (52 ml each) of nitroethane and deuterium oxide, and a catalytic amount of sodium acetate (about 0.2 g/100 ml of mixture), were stirred at reflux for 3 days. The aqueous layer was separated and washed with methylene chloride (2 × 10 ml). The organic layers were combined, dried (MgSO$_4$), filtered, and concentrated by distillation, and the product was distilled, bp 108–114°. The process was repeated two more times to give 26.7 g of product having 2% hydrogen and 98% deuterium at C(1) as determined by nmr spectroscopy.

Acetaldehyde-*1-d*$_1$.[25] Nitroethane-*1,1-d*$_2$ (26.7 g, 0.329 mol) from above was dissolved in ice-cold 10% sodium hydroxide solution (165 ml) and added to ice-cold sulfuric acid solution (50 ml of concentrated sulfuric acid in 330 ml of water) at such a rate that an ice–salt mixture maintained the temperature below 5°. The reaction mixture turned light blue and a gas (presumably NO) was evolved and led through a Dry Ice–acetone cold trap. After the addition was complete, nitrogen was bubbled through the reaction mixture and led to a cold trap assembly while the temperature was held at 75–85° for 2 hr. The trapped material was distilled from 50% sulfuric acid just prior to use in the next reaction, bp <33°. The yield was 5.52 g (37.3%) with 0.6% hydrogen and 99.4% deuterium at C(1) as determined by nmr spectroscopy.

(*Z*)-and (*E*)-1-(1-Deuterioethylidene)-2-methylcyclobutane (7-α-*d* and 8-α-*d*). To 125 ml of freshly distilled and dried tetrahydrofuran, phosphonium salt **11** (20.0 g, 0.0487 mol) was added. The mixture was stirred in a nitrogen atmosphere, the temperature was reduced to 5°, and *n*-butyllithium (35 ml, 1.4 *M*, 0.0490 mol) was added. To the resulting deep red solution, acetaldehyde-*1-d*$_1$ (2.8 ml, 0.0496 mol) was added and the mixture was allowed to stand overnight. The mixture was worked up in the same manner as was the undeuterated compound. The pot residue from the distillation (after a vacuum-line transfer) and two product-containing fractions provided 2.3 ml of product, which was further purified by preparative glpc (column B). Nmr spectra indicated 98.7% deuterium at the α position.

Kinetics of gas-phase isomerizations were determined using a modified version of a bath design suggested by Bergman and Shair (California Institute of Technology).

The system consisted of a well-seasoned 300-ml round-bottomed glass reaction vessel with a length of 9-mm glass tubing connected through a "greaseless" Teflon stopcock to a vacuum line. Inside the 9-mm tubing was a thermocouple well of 5-mm glass tubing which extended into the reaction vessel.

An aluminum cylinder 15.2 cm high × 17.6 cm in diameter was used as an air bath. The glass vessel was arranged in a close-fitting spherical cavity within the aluminum block using a split ring piece for a lid.

Heating was provided by eight cylinder heaters (GE 7C815A101, 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 $X(t + \Delta t) = X(t) + f[X(t) - (X(t - \Delta t) - X(t))/2]\Delta t$ 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 $A \rightarrow B \rightarrow C$ ($k_1 = 2 \times 10^{-5}$, $k_2 = 1 \times 10^{-5}$ 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]

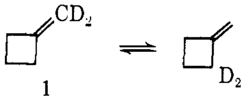
John E. Baldwin* and Ronald H. Fleming[2]

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** $\rightleftharpoons$ **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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