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.

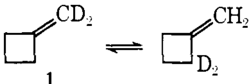
Thermal Rearrangements of Methylenecyclobutanes. Degenerate Rearrangement of Optically Active 1-(*Z*)-(1-Deuterioethylidene)-2-methyl-*trans*-3,4,4-trideuteriocyclobutane[1]

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

Contribution from the Department of Chemistry, University of Oregon, Eugene, Oregon 97403. *Received February 17, 1973*

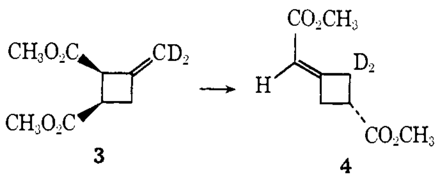
Abstract: 1-(*Z*)-(1-Deuterioethylidene)-2-methyl-*trans*-3,4,4-trideuteriocyclobutane at 332° isomerizes degenerately to give three other (*Z*)-1-ethylidene-2-methylcyclobutanes, one having the 3-deuterium label cis to the 2-methyl group, and the two cis–trans isomers of 1-ethylidene-2-methyl-2,3,4,4-tetradeuteriocyclobutane. 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

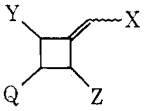


3 **4**

through resolution, then shown by nmr spectroscopy to have the deuterium label positioned as shown.[5]

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



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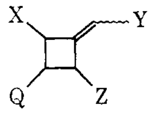

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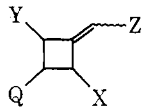

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of these three gross structures could exist in 16 isomeric forms, and hence thermal equilibration of one starting material could in principal lead to an equilibrium mixture of 48 isomers (24 *dl* pairs)!

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).

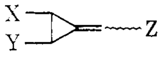
[5] W. von E. Doering, Lecture, 21st National Organic Chemistry Symposium of the American Chemical Society, Salt Lake City, Utah, June 1969.

materials leads to a grand total of 384 different rate constants, considering 1,3-sigmatropic shifts alone and recognizing that, by symmetry, mirror-image reactions would have identical rate constants. If one were to further allow interconversions among isomers within one structural set, as by epimerization at C(2), -(3), or -(4), or at C(2) and C(3) or at C(3) and C(4) simultaneously, another 120 rate constants would be involved in a complete description of the total system of 48 isomers.

Fortunately, not all of these rate constants would be independent: the 1,3-carbon migrations could be kinetically treated with 128 independent rate constants and 23 independent equilibrium constants. Considering isomerizations within a set would add another 60 independent rate constants.

Given these numbers, it is hardly surprising that no definitive kinetic work on the interconversion of labeled methylenecyclobutanes has appeared. It is a hard problem. Indeed, it is obvious that little progress may be made unless one happens upon a system in which the maximum complexity is avoided, and unless symmetry is exploited to the fullest possible extent.

(The degenerate methylenecyclopropane isomerization is far less complex, yet it too has escaped definitive kinetic and stereochemical specification. For the labeled system **8** (eight stereoisomers), 1,3-carbon migration could give stereoisomers of **9** and **10**. In all there are 192 rate constants for 1,3 shifts and 36 for epimerizations at C(2) or C(3) or at both simultaneously.



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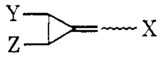

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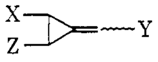

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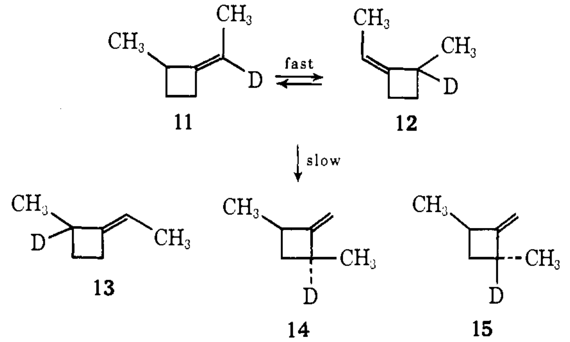
(There is some evidence that the 1,3 shift involves a well-defined stereochemistry,[6] with predominant[7] or at least some[8] net inversion at the migrating carbon. No experiments have been done to determine whether migration involves suprafacial or antarafacial allylic participation.)

The two suprafacial modes for the methylenecyclobutane automerization, according to one theoretical estimate, may be of comparable kinetic importance.[9,10]

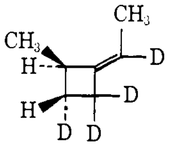
Through kinetic studies on the interconversions of the two isomers of 1-ethylidene-2-methylcyclobutane and the two isomers of 1-methylene-2,4-dimethylcyclobutane we learned that simple diradical intermediate models failed to accommodate the observed relative rate constants,[11] and that the *Z* isomer underwent degenerate rearrangement substantially faster than it suffered structural isomerization. Thus, it seemed an attractive substrate for more detailed stereochemical and kinetic work.

Our initial study with optically active (*Z*)-1-ethylidene-2-methylcyclobutane and 1-methylene-2-methylcyclobutane revealed both a component of the 1,3-sigmatropic carbon migration which utilized the allylic moiety antarafacially and a facile racemization without migration through epimerization at C(2).[12,13]

Thus, we had every reason to face the rigors of a more detailed stereochemically informative kinetic investigation, to place some quantitative measure on the component showing carbon 1,3 migration with antarafacial allylic participation. For although C(2) epimerization had become a definite complication to reckon with, we had a system, (*Z*)-1-ethylidene-2-methylcyclobutane, for which one degenerate isomerization was kinetically dominant. Since the deuterium scrambling **11** ⇌ **12** is significantly faster than isomerizations leading to the *E* isomer **13** or to the 1-methylene-2,4-dimethylcyclobutanes **14** and **15**, a stereochemically informative and tractable subset of all possible methylenecyclobutane isomerizations (504 direct and distinguishable first-order isomerizations and the same number of mirror-image reactions!) could be studied.



The selection of optically active and deuterium-labeled substrate **16**, 1-(*Z*)-(1-deuterioethylidene)-2-methyl-*trans*-3,4,4-trideuteriocyclobutane, as a suitable model for thorough kinetic investigation was made in the anticipation that it and its isomers **17**, **18**, and **19** would be different in nmr spectroscopic properties, permitting analyses of mixtures of the four by that technique.



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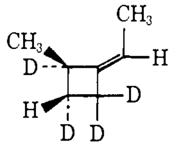

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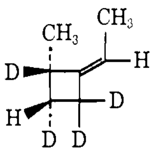

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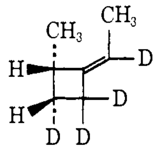

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Results

Synthesis of the required multiply labeled substrate was accomplished through the route outlined in Scheme I.

Reaction of ethyl (*E*)-crotonate with *m*-chloroperbenzoic acid in 1,2-dichloroethane[14] gave the corre-

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(6) E. F. Ullman, *J. Amer. Chem. Soc.*, **82**, 505 (1960).

(7) J. J. Gajewski, *ibid.*, **90**, 7178 (1968); **93**, 4450 (1971).

(8) W. von E. Doering and H. D. Roth, *Tetrahedron*, **26**, 2825 (1970); see also W. von E. Doering and L. Birladeanu, *Tetrahedron*, **29**, 499 (1973).

(9) J. A. Berson and L. Salem, *J. Amer. Chem. Soc.*, **94**, 8917 (1972).

(10) J. A. Berson, *Accounts Chem. Res.*, **5**, 406 (1972).

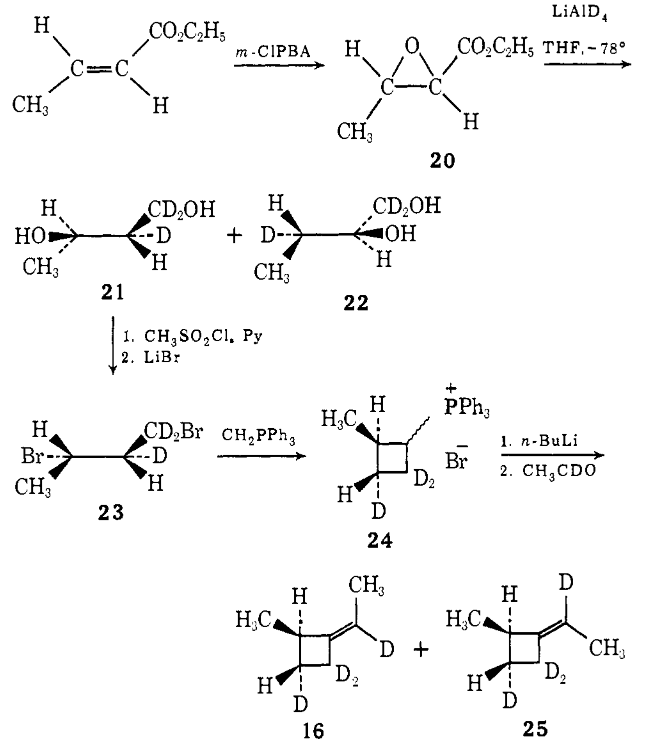
(11) J. E. Baldwin and R. H. Fleming, *J. Amer. Chem. Soc.*, **95**, 5251 (1973).

(12) J. E. Baldwin and R. H. Fleming, *ibid.*, **94**, 2140 (1972).

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

(14) L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis," Wiley, New York, N. Y., 1967, p 137.

Scheme I



sponding epoxide which, upon treatment with 3 equiv of lithium aluminum deuteride in tetrahydrofuran at −78°, gave a 3:1 mixture of diols **21** and **22**.

In trial experiments with lithium aluminum hydride, the ratio at room temperature was found to be less favorable, about 1.2:1.

The desired erythro isomer **21** was separated from the isomeric 1,2-diol through fractionation on a Teflon spinning band column, then converted by way of the dimethanesulfonate to the dibromide **23**,[15] with inversion at C(3).

Proton nmr spectra of dibromide **23**, taken with and without broad-band irradiation of deuterium nuclei, were indicative of a single stereoisomer.

From the dibromide, the cyclobutylphosphonium salt **24** was prepared in the normal manner,[11] purified through recrystallization, and converted to the stereochemically defined tetradeuterio derivatives **16** and **25** through Wittig reaction with deuterioacetaldehyde.

An nmr spectrum of the *Z* isomer **16**, taken with heteronuclear deuterium decoupling, showed that there had been a slight loss of stereochemical integrity during the Wittig sequence. Some 8% of isomer **19** contaminated the sample of **16**.

Optically active substrate (−)-**16** was obtained through selective destruction of (±)-**16** using an optically active hydroborating reagent.[16]

Racemic **16** was isomerized to **17**, **18**, and **19** at 332° and about 20 Torr pressure. The four *Z* isomers were isolated from the reaction mixture and purified by preparative glpc, then the relative amounts of each were determined by integration of the C(3) proton signal in the nmr spectra of the various samples pyrolyzed for different lengths of time. Compounds **16** and **19** showed C(3) doublets, but at different chemical shifts, while **17** and **18** showed singlets midway between the signals of each doublet. Note that without the deuterium labels at C(4) one would expect a complex multiplet corresponding to the proton at C(3). Even with the simplification due to substitution of deuterium at C(4), however, it was necessary to double irradiate the deuterons to get relatively sharp absorption signals. Table I lists the relative concentrations of **16**–**19** as determined by planimeter integration of each spectrum.

Table I. Product Ratios from the Pyrolysis of (±)-**16** at 332°

Time, 10^3 sec	**16**	**17**	**18**	**19**
0	0.916	0.0	0.0	0.084
5.3	0.786	0.068	0.026	0.120
10.4	0.681	0.130	0.048	0.140
17.0	0.608	0.137	0.079	0.176
21.9	0.564	0.189	0.078	0.169
28.9	0.503	0.194	0.126	0.177
41.8	0.457	0.209	0.163	0.171

The rate of racemization of optically active **16** was determined at 10–22 Torr pressure and 332°. The 95% confidence interval was 4.12 ± 0.46 × 10^{-5} sec^{-1}. The data are recorded in Table II.

Table II. Kinetic Data for Racemization of (−)-**16** at 332°

Time, 10^3 sec	$[\alpha]^{27°}_{222\text{ nm}}$ of **16** (deg)
0	−2040
7.54	−1550
18.6	−950
26.0	−711

One sample was run at a higher pressure than the others (22 Torr) for 18.6 × 10^3 sec; it provided material sufficient for both nmr analysis and measurements of optical activity. The degree of racemization, 46.6%, was consistent with the other racemization data in Table II. The nmr spectrum taken with broad band deuterium irradiation showed a singlet and a doublet for the C(2) methyl. By repeated integration using the instrument integrator, it was determined that the singlet constituted 30% of the total area and the doublet 70%. This corresponds to a deuterium scrambling rate of 4.92 × 10^{-5} sec^{-1}.

The C(3) proton signals in this sample are shown in Figure 1. From the relative intensities of doublets centered at δ 2.06 (J = 8.9 Hz) and 1.41 (J = 5.4 Hz), compared with the singlets between, the sample was estimated to have 28% deuterium at C(2), in fair agreement with the value based on C(2) methyl resonance integrations.

Discussion

The substrate **16** may give three isomers of the same structure and configuration, each detectable by nmr spectroscopy. The kinetic scheme appropriate for analyzing the raw data of Table I is shown in Scheme II.

In terms of this scheme and neglecting isotope

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(15) L. A. Paquette and J. P. Freeman, *J. Org. Chem.*, **35**, 2249 (1970).

(16) H. C. Brown, N. R. Ayyanger, and G. Zweifel, *J. Amer. Chem. Soc.*, **86**, 397 (1964).

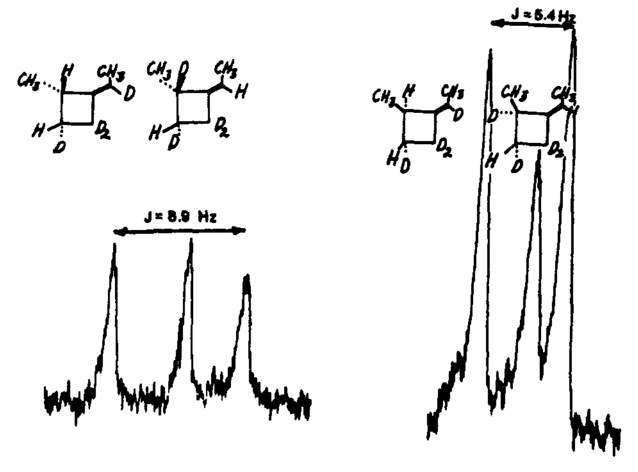
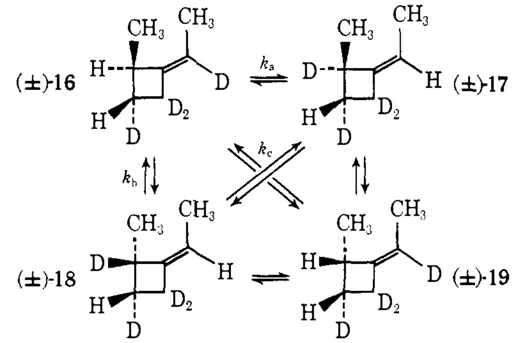


Figure 1. Proton nmr spectrum with deuterium decoupling of **16–19** from pyrolysis of (−)-**16** for 18.6 × 10³ sec at 332°.

Scheme II



effects, all four rate constants related to horizontal arrows are k_a; all four with vertical arrows are k_b; all four diagonal arrows are for first-order isomerizations with rate constant k_c.

In terms of this 12-rate constant scheme, the best three-parameter fit to the experimental data of Table I was found with the aid of a computer.[11] The rate constants obtained were $k_a = 1.36$, $k_b = 0.40$, and $k_c = 0.86$, all $\times 10^{-5}$ sec^{-1}.

Using this scheme and these rate constants, the concentrations of the four compounds were calculated as a function of time and are displayed in Figure 2 along with the experimentally determined points.

The kinetic work leading to the rate constants k_a, k_b, and k_c and the thermolysis of optically active **16** which gave a direct, same-sample comparison for the isomerizations observable by nmr ($k_{ds} = 4.92 \times 10^{-5}$ sec^{-1}) and by polarimetry ($k_\alpha = 4.12 \times 10^{-5}$ sec^{-1}) were done weeks apart. The rate constant for deuterium scrambling, $k_{ds} = 4.92 \times 10^{-5}$ sec^{-1}, and the value calculated from k_a and k_b, 3.52×10^{-5} sec^{-1}, show a discrepancy of about one-third. Such a small variation might be caused by a slight difference in bath temperature and/or systematic errors associated with determinations of k_a, k_b, and k_c through planimetry and computer-aided best-fit techniques. To put k_a, k_b, and k_c on a scale suitable for comparisons including k_α, they were multiplied by 4.92/3.52 to give $k_a' = 1.9$, $k_b' = 0.56$, and $k_c' = 1.2$, all $\times 10^{-5}$ sec^{-1}. Thus, the rate constants k_a, k_b, and k_c were taken as a fair guide to relative rate behavior, and were augmented by the same small proportionality factor.

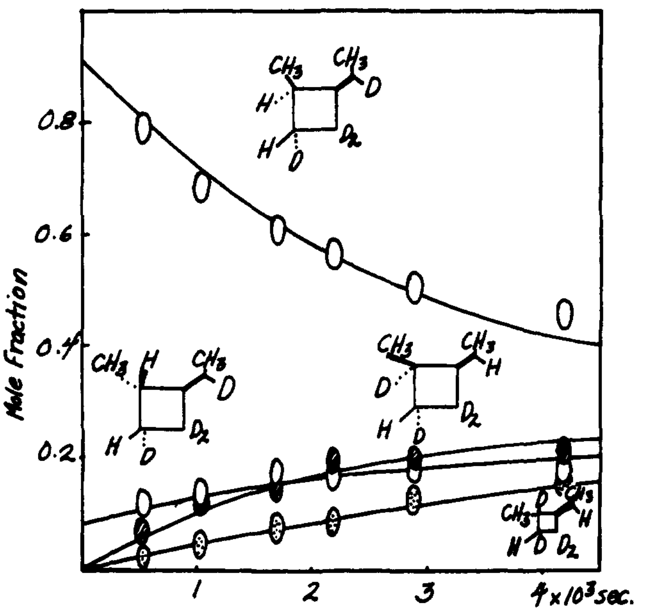


Figure 2. Experimental points and calculated lines for the mole fractions of **16–19** from the pyrolysis of **16** at 332°.

While the successful reduction of the 28 data points in Table I from six separate kinetic runs to three independent rate constants (Figure 2) implies that the experiments are reliable and reproducible, the discrepancy between $2(k_a + k_b)$ and the k_{ds} value determined later with the large optically active sample of **16** raises a legitimate concern: the augmentation of k_a, k_b, and k_c by the scaling factor 1.37 to make them comparable with k_α may simply compensate for an inability to reestablish bath temperature at 332° with sufficient accuracy, but some test of the scaling process seemed essential.

Fortunately, the large sample giving k_{ds} and a k_α point also provided a direct test of the scaling procedure: the theoretical curves of Figure 2, if the procedure is justified, should be valid for the large sample heated (at presumably a somewhat higher temperature) for 18.6×10^3 sec—but the evaluation ought to be done at $18.6 \times 1.37 \times 10^3$ sec. The predicted and experimental mole fractions are listed in Table III.

Table III. Theoretical and Experimental Isomer Ratios from the Pyrolysis of (−)-**16** at 332° for 18.6 × 10³ sec

Isomer	Calcd[a]	Exptl[b]
16	0.53	0.55
17	0.19	0.19
18	0.11	0.09
19	0.17	0.17

[a] From curves in Figure 2, at 25.5 × 10³ sec. [b] From relative integrated absorption intensities of the C-3-H resonances.

The agreement is well within likely experimental errors, and the scaling procedure adopted is seen to give consistent results: the single sample on which both optical activity and the ratios of isomers **16–19** were determined was in experimental agreement with predictions based on the equally augmented rate constants k_a', k_b', and k_c'.

The choice of system **16** was strongly influenced by a desire to learn something more about the stereochemistry of methylenecyclobutane isomerizations without recourse to highly resolved starting material or to resolution of product enantiomers. But the full complexity of the interconverting system must be considered in assessing the experimental data, so that no stereochemical option is carelessly ignored. Thus, one must keep in mind the four isomers **16**, **17**, **18**, and **19** and their mirror images.

The experimental rate constants are related to rate constants for individual conversions then by the following equations:

$$k_a' = k_{ra} + k_{is} = 1.9 \times 10^{-5}$$

$$k_b' = k_{rs} + k_{ia} = 0.56 \times 10^{-5}$$

$$k_c' = k_{2e} + k_{3e} = 1.2 \times 10^{-5}$$

$$k_\alpha = 2(k_{is} + k_{rs} + k_{2e} + k_{23e}) = 4.12 \times 10^{-5}$$

The subscripts r (retention), i (inversion), s (suprafaciation), and a (antarafaciation) refer to the stereochemistry of the 1,3-carbon migration. Since the rate constant k_a' measures $k_{ra} + k_{is}$, the two allowed modes, and k_b' is $k_{rs} + k_{ia}$, the two stereochemical outcomes classed as disallowed by orbital symmetry theory, one has a direct measure of this distinction: the 1,3-carbon migration occurs with an allowed to disallowed stereochemical ratio of 1.9:0.56, or 77:23.

The rate constants k_{2e} and k_{3e} stand for direct epimerization at C(2) and C(3), respectively. The known epimerization at C(2) in 1-methylene-2-methylcyclobutane[13] leads one to expect it would be competitive here too.

The rate of racemization is a composite of both suprafacial carbon migration modes, epimerization at C(2), and simultaneous epimerization at C(2) and C(3) (rate constant: k_{23e}). The k_{23e} process would not be detected by the nmr measurements, but might contribute to racemization.

With seven individual rate constants leading from any member of the set **16**, **17**, **18**, **19** plus the four mirror images to the others, the four experimentally observed kinetic components of automerization can provide no unique solution.

Thus, even though this may be the most extensively dissected thermal hydrocarbon automerization reported to date, wherein four rate processes interconverting isomers identical but for deuterium labels and optical activity have been quantified, an assumption-free reduction of all the data to stereochemical terms is not possible.

At one extreme, with maximum antarafacial 1,3-carbon migration, the experimental results might be fitted by the solution $k_{ra} = 1.9$, $k_{ia} = 0.56$, $k_{2e} + k_{3e} = 1.2$, and $k_{2e} + k_{23e} = 2.06$, all $\times 10^{-5}$ sec^{-1}. Thus 100% of the 1,3-carbon shift might be antarafacial.

At the other extreme, with minimum antarafacial 1,3-carbon migration, the data can be satisfied by $k_{ra} + k_{ia} = 0.40$, $k_{ra} + k_{is} = 2.06$, $k_{2e} + k_{23e} = 0$, and $k_{3e} = 1.2$. Thus only 16% of the 1,3-carbon migration has to be antarafacial.

Both of these extreme solutions permitted by the data are probably wrong. There are too many cases of suprafacial 1,3-carbon migration and too few cases of migration in the inversion-antarafacial stereochemical sense to imagine that the 1,3 shift goes 77% ra and 23% ia. And the sure experimental determination of thermal epimerization at C(2) in 1-methylene-2-methylcyclobutane[13] makes it highly unlikely that in the present case $k_{2e} + k_{23e} = 0$. Hence, less than 100% and more than 16% of the carbon shift is likely to be antarafacial.

Another and less extreme fit to the data may be made based on the assumption that there is no direct thermal epimerization at C(3) ($k_{3e} = 0$). Then $k_{ra} + k_{ia} = 1.60 \times 10^{-5}$ sec^{-1} $+ k_{23e}$, *or at least 65% of the 1,3-carbon shift is antarafacial.* Only when $k_{3e} > k_{23e}$ can less than 65% of the shift be antarafacial. This is a conceivable situation—k_{3e} in this system might be equivalent to k_{34e}, and k_{34e} might be faster than k_{23e}; but it does not seem particularly likely. Further experimental work will be necessary to settle the issue.

If it turns out that $k_{3e} < k_{23e}$ and/or that both are much smaller than k_{2e}, the retention-antarafacial stereochemistry for the 1,3-carbon shift in the degenerate methylenecyclobutane rearrangement will be recognized as the dominant mode, in striking conformation of the predictive scope of orbital symmetry theory.[17,18]

Experimental Section

The instruments and kinetic methods used have been detailed.[11] Preparative glpc separations were done on 5 or 6 m × 6 mm 20% β,β'-oxydipropionitrile on 60–80 Chromosorb P columns at 50–80°.

Ethyl (*E*)-2,3-Oxidobutyrate (20).[14] Ethyl (*E*)-crotonate (56.1 g, 0.492 mol) and 85% *m*-chloroperbenzoic acid (100 g, 0.492 mol) were stirred at reflux in 1,2-dichloroethane for 4 hr. More *m*-chloroperbenzoic acid (25 g, 0.123 mol) was added and the mixture was heated at reflux for 2.5 hr. The mixture was cooled to room temperature and treated with sodium bicarbonate (100 g in 1.0 l. of water). Enough sodium sulfite was added to cause a negative starch–iodide paper test. The organic layer was separated, washed with water (2 × 1.0 l) and brine (1 × 200 ml), dried ($MgSO_4$), filtered, and concentrated by distillation. Spinning band fractionation gave 41.8 g (65.3%) of product, bp 106.5° (73 mm).

***erythro*-1,3-Butanediol-*1,1,2-d*$_3$ (21).** Lithium aluminum deuteride (10.6 g, 0.252 mol) was placed in a dry 1-l. flask. Tetrahydrofuran (600 ml) was distilled from lithium aluminum hydride directly into the flask, a dry nitrogen atmosphere was provided, and the temperature was reduced to −78°. To the stirred mixture, ethyl (*E*)-2,3-oxidobutyrate (41.4 g, 0.318 mol) was added over a period of 2 hr. The temperature was maintained at −78° for 4 hr followed by 24 hr at room temperature. Sodium hydroxide solution (15%, 10 ml) and water (15 ml) were added. The mixture was filtered, dried ($MgSO_4$), filtered, and concentrated at reduced pressure. The residue was fractionated on a spinning band column to give 10.41 g of product **21**, bp 139° (57 mm). An additional portion (1.38 g) was recovered from the pot residue by vacuum transfer. Three fractions (6.28 g) of impure product and by-product (mainly 1,2-butanediol-*1,1,3-d*$_3$, **22**), bp 121–138° (57 mm), were also obtained. The total yield was 18.07 g, 61%. The nmr spectra of both isomers showed the expected similarities to authentic perprotio samples.

***erythro*-1,3-Butanediol-*1,1,2-d*$_3$ Dimethanesulfonate.**[15] To a stirred solution of 1,3-butanediol-*1,1,2-d*$_3$ (11.79 g, 0.127 mol) in dry pyridine (50 ml) at −15 to −12°, methanesulfonyl chloride (29.0 g, 0.254 mol) was added over a period of 40 min. The mixture was stored at −18° for 20 hr, then poured over twice its volume of crushed ice; the resulting mixture was extracted with methylene chloride (3 × 75 ml). Ice-cold 5% hydrochloric acid was added until the aqueous layer remained acidic. The organic phase was separated, dried ($MgSO_4$), filtered, and concentrated at reduced pressure to give a yellow oil suitable for further reaction.

***threo*-1,3-Dibromobutane-*1,1,2-d*$_3$ (23).**[15] The crude 1,3-butanediol-*1,1,2-d*$_3$ dimethanesulfonate from above, lithium bromide

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

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

(dried for 2 days *in vacuo* over calcium sulfate; 52 g, 0.6 mol), and dry dioxane (250 ml) were stirred at reflux for 13 hr. The mixture was cooled, poured into ice–water (300 ml), and extracted with pentane (4 × 75 ml). The pentane fractions were combined and washed with ice–water (2 × 100 ml), and the combined aqueous portions were extracted with pentane (1 × 75 ml). The organic phase and the other organic portions were combined, dried (MgSO$_4$), filtered, and concentrated at reduced pressure; the residue was distilled to give 21.8 g (78.6% from the diol) of product **23**, bp 57–61° (21 mm). The nmr spectrum (CHCl$_3$) showed a doublet at δ 1.74 (3 H, $J = 6.8$ Hz), a broad signal, 2.20 (1 H), and a symmetrical multiplet, 4.29 (1 H). Upon broad band deuterium irradiation, the signal at δ 2.20 became a doublet, $J = 3.8$ Hz; the signal at δ 4.29 became a quartet, $J = 6.8$ Hz, of doublets, $J = 3.8$ Hz.

(2-*r*-Methyl-*trans*-3,4,4-trideuteriocyclobutyl)triphenylphosphonium Bromide (24).[11,19] Sodium hydride (5.57 g, 0.232 mol, 9.80 g of 57% suspension in mineral oil) was washed with pentane (3 × 20 ml). Tetrahydrofuran (450 ml) and methyltriphenylphosphonium bromide (68.8 g, 0.193 mol, 70.3 g of 98% pure material) were added and the mixture was stirred 9 hr under a nitrogen atmosphere at 50–54°. Solid materials were allowed to settle and the orange supernatant was forced through a glass tube into an oxygen-free flask using nitrogen pressure. *threo*-1,3-Dibromobutane-*1,1,2*-d_3 (21.5 g, 0.0981 mol) from above was added dropwise while holding the temperature below 30°. The mixture was stirred 24 hr at 50–54°, allowed to cool, and filtered. Solvent was removed from the solid *in vacuo*; the material was recrystallized from water (69 ml) and dried *in vacuo* at 58° over calcium sulfate to give 18.3 g of product (45.5%), mp 233–250°.

1-(*Z*)-(1-Deuterioethylidene)-2-methyl-*trans*-3,4,4-trideuteriocyclobutane (16).[11] The phosphonium bromide **24** (18.3 g, 0.0442 mol), tetrahydrofuran (150 ml), and *n*-butyllithium (15.14% in hexane, 27.8 ml, 0.0530 mol) were stirred at room temperature for 1 hr under a nitrogen atmosphere. Acetaldehyde-*1*-d_1 (2.6 g, 0.057 mol) was added and the mixture was allowed to stir overnight. Ice–water (250 ml) and pentane (50 ml) were added; the aqueous layer and the solid residue were removed and washed with pentane (25 ml). The pentane fractions were combined and washed with ice–water (250 ml), at which point more solids precipitated. The aqueous layer and solid material were washed with pentane (25 ml), and all the pentane layers were combined and washed with ice–water (7 × 250 ml), dried (MgSO$_4$), filtered, and concentrated by spinning band distillation. A forerun (bp 84–94°, 0.292 g of the products, 45% pure by glpc) was taken followed by the main fraction (bp 94–98°, 1.358 g, 96% pure). After vacuum transfer, the pot residue consisted mainly of 1-ethylidene-2-methylcyclobutane products (1.058 g, 96% pure). The total yield was 2.43 g (55.0%) of a mixture of isomers (**16** and **25**) which could be separated by preparative glpc. With broad band deuterium irradiation the nmr spectrum of the longer retention time *Z* product **16** showed a doublet, $J = 7.0$ Hz, 1.19 (C(2) methyl); a doublet, $J = 5.4$ Hz, δ 1.41 (C(3) proton); a doublet, $J = 1.5$ Hz, δ 1.51 (vinylic methyl); and a quintet, $J = 7.0$ Hz, of quartets, $J = 1.5$ Hz, δ 3.01 (C(2)). A small amount (8.4%) of **19** with C(3) hydrogen trans to the methyl was present as indicated by the doublet, $J = 8.9$ Hz, δ 2.06.

Partial Resolution of 1-(*Z*)-(1-Deuterioethylidene)-2-methyl-*trans*-3,4,4-trideuteriocyclobutane.[16] Sodium borohydride (71.2 mg, 1.875 mmol), (−)-α-pinene ($[\alpha]^{23°}_{\mathrm{D}}$ −47.6; 680 mg, 5.00 mmol), and diglyme (2.0 ml) were stirred under a nitrogen atmosphere. The temperature was lowered to 0° and boron trifluoride etherate (355 mg, 2.50 mmol) in diglyme (5.8 ml) was added dropwise over 10 min. After 4 hr at 0°, the olefin, **16** (522 mg, 5.22 mmol), was added. The reaction mixture was allowed to stand overnight. It was then diluted with ice–water (25 ml) and extracted with pentane (3 × 25 ml). The pentane layers were combined, washed with ice–water (3 × 25 ml), and dried (MgSO$_4$); the solution was filtered and concentrated by spinning band distillation. Vacuum transfer and preparative glpc of the pot residue gave 157 mg of product (60.3%), $[\alpha]^{27°}_{222\mathrm{nm}}$ −2040° (gas phase).

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(19) *Cf.* E. L. Eliel, *J. Chem. Educ.*, **48**, 163 (1971).

Solvolytic Rearrangement of 1,2,3-Tri-*tert*-butyl-3-dichloromethylcyclopropene and *cis*-3,4-Dichloro-1,2,3-tri-*tert*-butylcyclobutene[1]

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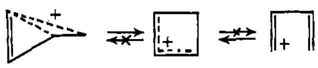
Contribution from the Metcalf Research Laboratories, Brown University, Providence, Rhode Island 02912. *Received March 2, 1973*

Abstract: Reaction of tri-*tert*-butylcyclopropenyl fluoroborate (**9**) with dichloromethyllithium at low temperature gave 1,2,3-tri-*tert*-butyl-3-dichloromethylcyclopropene (**6**). Compound **6** underwent facile isomerization to *cis*-3,4-dichloro-1,2,3-tri-*tert*-butylcyclobutene (**7**). Reduction of **7** with lithium aluminum hydride afforded 1,2,3-tri-*tert*-butylcyclobutene (**12**). Reaction of **7** with *tert*-butyllithium produced 1,2,3,4-tetra-*tert*-butylcyclobutene (**13**) and **12**. Tri-*tert*-butylcyclobutadieneiron tricarbonyl (**14**) was prepared by the reaction of diiron nonacarbonyl with **7**. Dichlorides **6** and **7** were found to undergo a novel solvolytic rearrangement in aqueous dioxane to 1,2-di-*tert*-butyl-3-pivaloylcyclopropene (**8**). Treatment of **8** with phosphorus pentachloride resulted in the formation of dichloride **7**. Kinetic data indicated that **6** is 28 times more reactive than **7** toward solvolysis. The results are consistent with an ionic mechanism involving cyclobutenyl cation **10** as a common intermediate.

The generation of carbonium ions within the framework of highly strained molecules is frequently accompanied by a complex series of σ bond rearrangements. Almost alone among small rings, the cyclobutenyl cation (**1**) normally shows little tendency to undergo such rearrangements. Indeed **1** should lie at the position of minimum energy with respect to its isomers such as the bicyclobutenium ion (unsaturated bicyclobutonium ion) **2** or vinyl cation **3**.



2 **1** **3**

The bicyclobutenium ion **2**, generated by the sol-

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[1] For a preliminary communication, see J. Ciabattoni and A. E. Feiring, *J. Amer. Chem. Soc.*, **94**, 5113 (1972).

[2] Abstracted from the Ph.D. Thesis of A. E. Feiring, Brown University, 1973. National Science Foundation Graduate Trainee, 1970–1971.