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STEREOCHEMISTRY OF THE THERMAL ISOMERIZATIONS OF (2*S*,3*R*)-2-METHOXYMETHYL-2,3-DIDEUTERIO-1-(DIDEUTERIOMETHYLENE)CYCLOPROPANE

JOHN E. BALDWIN* and GLENN EU CHUNG CHANG
Department of Chemistry, University of Oregon, Eugene, OR 97403, U.S.A.

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Abstract—The (2*S*,3*R*) isomer of 2-methoxymethyl-2,3-dideuterio-1-(dideuteriomethylene)cyclopropane has been synthesized and heated at 198.8°: from the experimentally observed mol fractions of the eight isomers of 2,3,α,α,- and 2,3,3,α - tetradeuterio - 2 - methoxymethyl - 1 - methylenecyclopropane in the pyrolysis product mixture have been derived rate constants for seven distinct modes of isomerization. One-center thermal epimerizations at C(2) and C(3) and the C(2)C(3) two-center epimerization are of kinetic importance. Only two of four observable stereochemical modes for carbon [1,3] shifts are seen: there is inversion of stereochemistry at the migrating C atom, while the C(3)H *trans* to C(2)–CH_2OCH_3 in starting material becomes *anti* : *syn* 4 : 1 C(α)-H in the [1,3] shift product. Stereomutation at C(2) does not occur along the reaction coordinate for [1,3] carbon shifts.

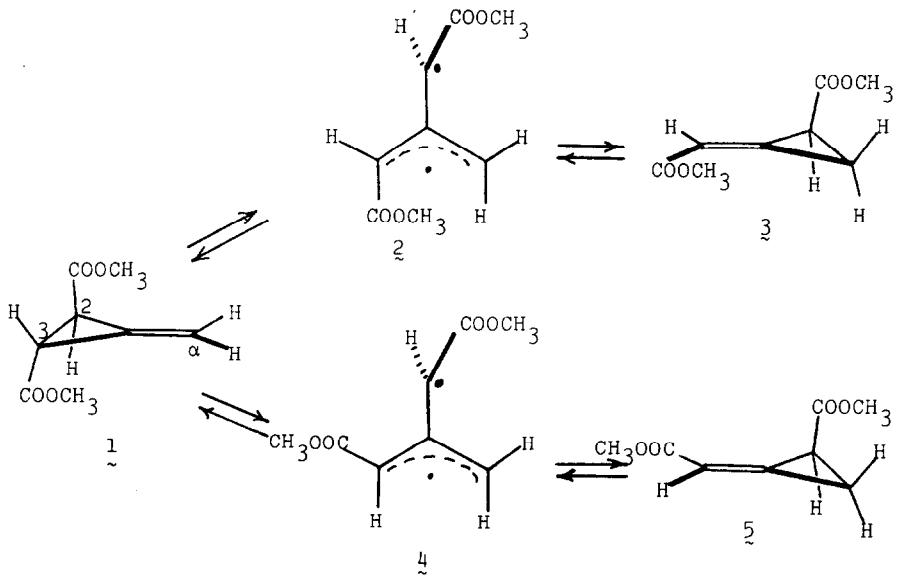
The thermal conversion of one methylenecyclopropane to another through a [1,3]-sigmatropic transformation, first observed in 1932[1] and first formulated in proper structural terms in 1952,[2] has become a well-recognized archetypical molecular rearrangement.[3,4]

The stereochemical course of the [1,3]-carbon migration has been probed experimentally and theoretically. The [1,3]-shift of C(2) or C(3) to the exocyclic C(α) of a methylenecyclopropane is known to proceed with considerable stereoselectivity[5] and to involve net inversion at the migrating, or "pivot", carbon.[6,7] These stereochemical facts are compatible with rearrangement by way of perpendicular diradical intermediates or activated complexes. The isomerization of (+)-(*R*) Feist's ester **1** to products **3** and **5** with diradicals **2** and **4** as putative intermediates illustrates this compatibility. The *anti*-isomer **3** is kinetically favored over the *syn* alternative **5** by a ratio of about 3.7 : 1, while the *syn* structure is favored thermodynamically.[6]

The hypothetical intermediates or transition state structures **2** and **4** are perpendicular diradicals: an allylic moiety and a unique methylene group are joined by a C–C single bond and oriented orthogonally.

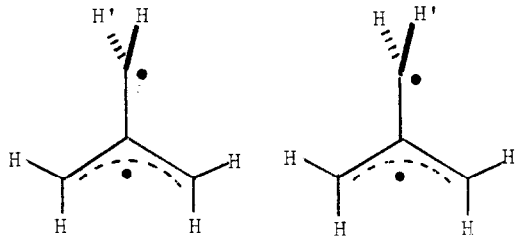
If methylenecyclopropanes isomerized only through the [1,3]-shift of C(2) to give a unique product, as in **1**→**3**, the stereochemical aspects of such thermal rearrangements would probably be known today in full quantitative detail: the extent of stereoselectivity shown by the migrating C(2) and the attendant stereochemical events at C(3) and C(α) would have been firmly established for representative cases of the isomerization. The kinetic situation is not so simple, though, and the experimental definition of reaction stereochemistry for the methylenecyclopropane rearrangement remains incomplete for quite understandable reasons.

A methylenecyclopropane with different stereochemical labels at C(α), C(2), and C(3) would be one of 24 distinct isomers. The [1,3]-shifts of C(2) and C(3),[8–11]

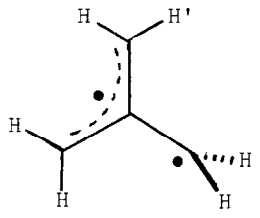


thermal stereomutations at C(2) and C(3),[8-11] and *cis–trans* isomerization at C(α) would convert a single stereochemically well-defined isomer into a complex mixture of products, and the initial products would also exhibit both thermal stereomutations and carbon [1,3]-shifts. To unravel this complex stereochemical problem and derive rate constants linking each isomer with the 23 others would be a formidable experimental and analytical task, even though some of the rate constants might be negligible and others would be constrained by microscopic reversibility and would not be independent parameters.

Theoretical approaches to the stereochemistry of the methylenecyclopropane rearrangement have concentrated on the [1,3]-carbon migration.[12,13] Several methodologies have been applied to the rearrangement and various conclusions have been reached. Many support the C_{2v}-symmetric diradical intermediate **6** for the parent and fully degenerate C_4H_6 case, though estimates of the depth of the local energy minimum differ widely. Isomerization of the methylene-allylic diradical through simple rotation about one C–C bond (**6**→**7**) or through geometric exchange of the symmetry-unique methylene group (**6**→**8**) are predicted to be fairly facile processes. Dixon *et al.*, for instance, estimate barriers of only 1.8 and 2.8 kcal/mol for these two isomerizations.[12]



6 7



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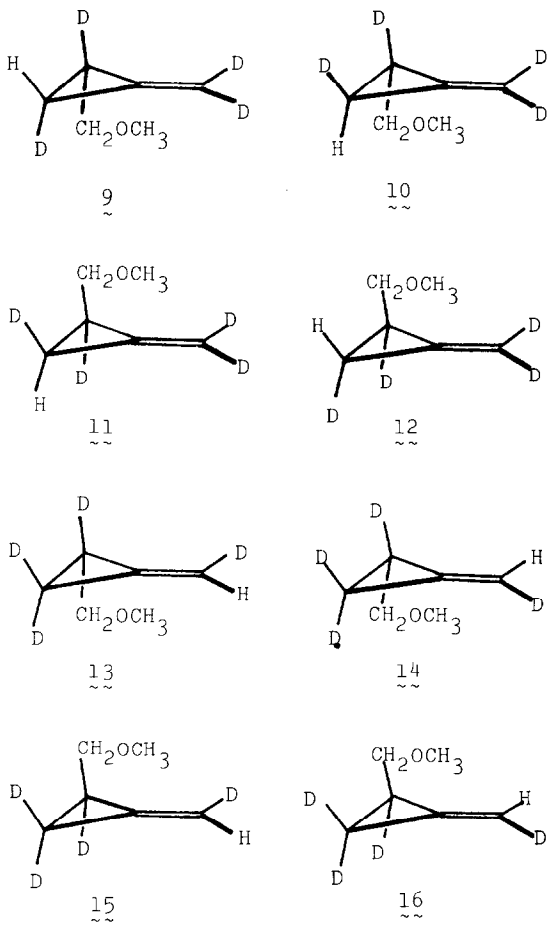
Constructive dialog between experimentalists and theoreticians interested in the methylenecyclopropane rearrangement has been limited by a relative dearth of sufficiently detailed stereochemical information and of calculations on other than the unsubstituted C_4H_6 case which would lead to experimentally testable stereochemical predictions.

RESULTS

To determine more completely the stereochemical characteristics of methylenecyclopropane rearrangements, an optically active 2 - methoxymethyl - 2,3 - dideuterio - 1 - (dideuteriomethylene)cyclopropane was prepared and a kinetic investigation of the degenerate thermal isomerizations it exhibited was undertaken.

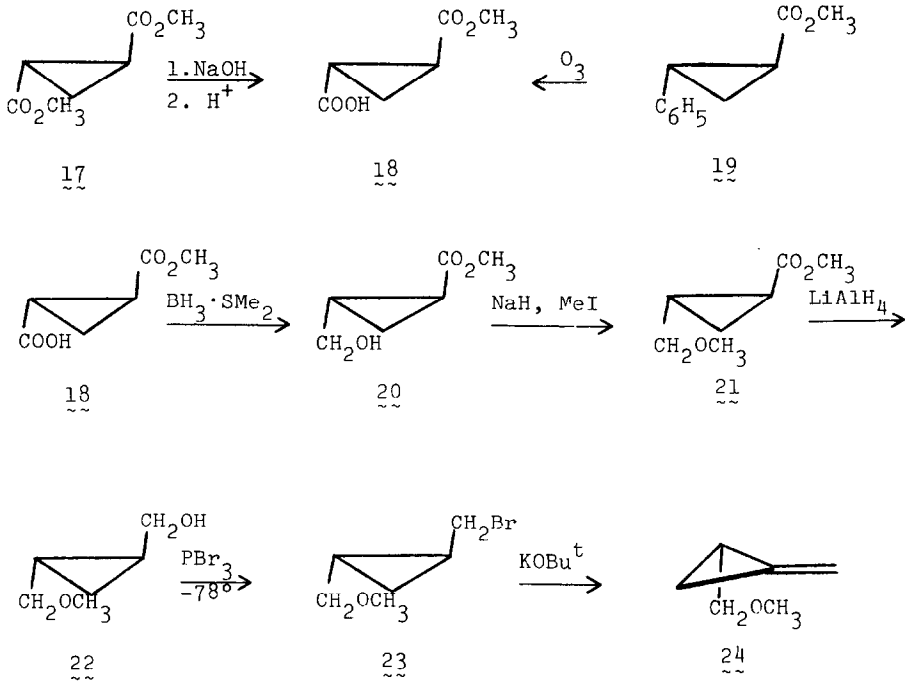
This particular methylenecyclopropane system was selected for investigation because it seemed to offer an attractive compromise between stereochemical complexity and analytical accessibility. Interconversions among the eight isomers **9**–**16** would be constrained by microscopic reversibility so that the time evolution of the system could be described by at most nine independent rate constants. These nine rate constants will be called k_2, which is identical with the specific rate constants **k(9→12)**, **k(10→11)**, **k(11→10)**, and **k(12→9)**; k_3, which is for example equivalent to **k(9→10)**; k_{23} = **k(9→11)**; k_r = **k(9→13)**; k_i = **k(9→15)**; k_r' = **k(9→14)**; k_i' = **k(9→16)**; k_{sa} = **k(13→14)**; and k_{sa}' = **k(13→16)**. For convenience, $k_{13} = k_r + k_i$ and $k_{13}' = k_r' + k_i'$. All other rate constants relating one of the eight isomers to another in the set are equal to one of these nine independent rate constants, or a simple combination thereof; **k(13→15)** for instance, is equal to $k_2 + k_{23}$. The mixture of isomers **9**–**16** could be analyzed, it was hoped, by NMR spectroscopy with the aid of chiral shift reagents.[14] Further, the (2*S*,3*R*) and (2*S*,3*S*) isomers **9** and **10** might be prepared from deuterium-labeled chiral intermediates we had employed in previous work, thus offering a potential economy of synthetic effort.[15]



9 10 11 12 13 14 15 16

The synthetic route was first developed with unlabeled racemic compounds as outlined in Scheme I.

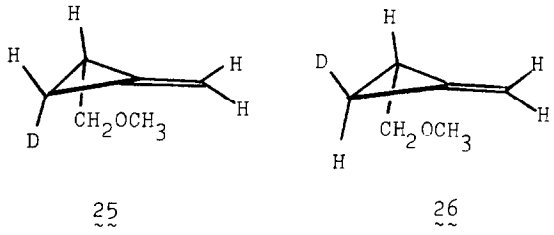
trans - 2 - Carbomethoxycyclopropanecarboxylic acid **18** was made from commerical diethyl *trans* - 1,2 - cyclopropanedicarboxylate through transesterification with methanol followed by partial saponification of



Scheme I.

dimethyl ester **17**;[16,17] it was also made from methyl *trans*-2-phenylcyclopropanecarboxylate **19** through oxidation of the phenyl substituent with ozone.[18] Selective reduction of the carboxylic acid function with borane-dimethyl sulfide[19] gave alcohol-ester **20** and methylation of the hydroxymethyl group of **20** afforded the methyl ether methyl ester **21**. Reduction of the ester with lithium aluminum hydride[20] gave the cyclopropylcarbinol **22**, which was converted with phosphorus tribromide[21] in ether at −78° to the cyclopropylcarbinyl bromide **23**. Dehydrohalogenation of the bromide with potassium t-butoxide in dimethyl sulfoxide gave the racemic 2 - methoxymethyl - 1 - methylenecyclopropane **24**.

Racemic samples of the 2 - methoxymethyl - 3 - deuterio - 1 - methylenecyclopropanes **25**+**26**, 2 - methoxymethyl - *trans* - 2,3 - dideuterio - 1 - (dideuteriomethylene)cyclopropane **9**+**11**, and 2 - methoxymethyl - *cis* - 2,3 - dideuterio - 1 - (dideuteriomethylene)cyclopropane **10**+**12** were prepared[15] from β-deuteriostyrene (80:18 *cis*:*trans*), *trans*-α,β-dideuteriostyrene, and *cis*-α,β-dideuteriostyrene, through condensations with ethyl diazoacetate followed by the sequence of steps in Scheme I.



25 **26**

Trial pyrolyses of **25**+**26** provided rough estimates of the extent of epimerization at C(3) and of [1,3]-carbon shifts as a function of temperature, and led to the conclusion that a bath temperature near 200° would be convenient. All further work was done at 198.8°.

Pyrolyses of **9**+**11** or **10**+**12** gave mixtures which included the 2,3,3,α-tetradeuterio isomers **13**–**16**. The chemical shifts of the singlet proton absorptions for the racemic materials in perdeuteriobenzene were observed at δ 1.1 (*trans* isomer: **9**+**11**); 0.8 (*cis*: **10**+**12**); 5.5 (*anti*: **13**+**15**); and 5.6 ppm (*syn*: **14**+**16**) (Fig. 1).

The assignment of the cleanly separated vinylic C(α) proton singlets at 5.5 and 5.6 ppm to *anti* (**13**+**15**) and *syn* (**14**+**16**) isomers, respectively, was based on their different behavior in the presence of the chiral NMR shift reagent tris(3 - heptafluorobutyryl - *d* - camphorato)europium(III), Eu(hfbc)$_3$;[22] the more downfield singlet in the vinyl region was shifted further downfield and at a greater rate than the upfield singlet with added shift

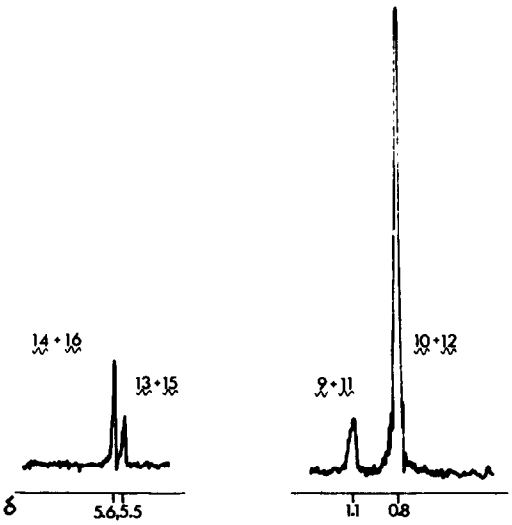


Fig. 1. Distinct NMR singlets for vinyl and ring protons in a mixture of isomers **9**–**16** derived from 120-min. thermolysis of *dl* *cis* substrate (**10**+**12**).

reagent. The C(α) proton *syn* to the methoxymethyl group which complexes the shift reagent would be expected to show the more pronounced downfield shift with added Eu(hfbc)$_3$. At high concentrations of shift reagent, the enantiotopically distinct vinyl protons could all be distinguished (Fig. 2).

In the presence of Eu(hfbc)$_3$, the enantiotopic methoxy singlets for the methylenecyclopropanes **9–16** were well separated, as were the C(3)-H enantiotopic singlets for isomers **10** and **12** (Fig. 3). When optically active substrates were prepared, the assignments indicated in Fig. 3 could be made (see below).

Fig. 2. Enantiotopically distinct vinyl proton absorptions in the presence of Eu(hfbc)$_3$, demonstrated with a recemic mixture of **25** and **26**.

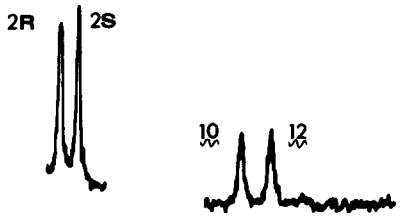
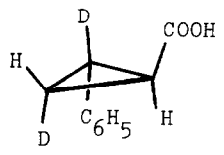


Fig. 3. Resolution of enantiotopic methoxy singlets (left) and C(3)-H singlets (right) in racemic substrates **10**+**12** in the presence of Eu(hfbc)$_3$.

Optically pure[23] and specifically deuterated *trans* - 2 - phenylcyclopropanecarboxylic acids such as the (+)-(1*S*,2*S*,3*R*) and the (+)-(1*S*,2*S*,3*S*) isomers **27** and **28** may be prepared conveniently through the reaction of *dl*-menthyl diazoacetate[24] with *trans* or *cis*-α,β-dideuteriostyrene[25,26] in the presence of the chiral copper catalyst **29** derived from D-alanine.[27] This reaction gives a mixture of esters in 50–60% yield, with a *trans*:*cis* ratio of 85 : 15, and the *trans* isomer is 70–80% optically pure. A single recrystallization of the quinine salt of the corresponding acid[18] leads to optically pure **27** or **28**.



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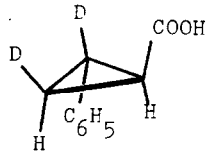

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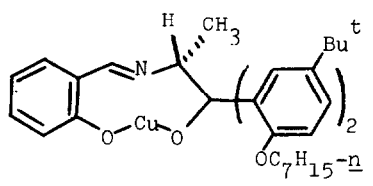

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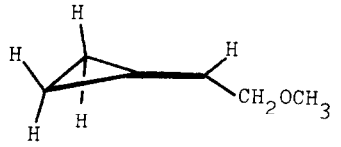
The synthetic route of Scheme I, with LiAlD$_4$ in place of LiAlH$_4$, converts the methyl ester of **27** to (2*S*,3*R*) - 2 - methoxymethyl - 2,3 - dideuterio - 1 - (dideuteriomethylene)cyclopropane **9** and some isomeric impurities. While the dideuteriostyrene from which **9** was made was estimated by NMR to be 97% *trans*, and the intermediate acid **27** was optically pure as judged by NMR analysis of its methyl ester with the aid of chiral shift reagent Eu(Opt),[28] the synthetic product **9** was found to be 92% optically pure according to analysis with the chiral shift reagent Eu(hfbc)$_3$ through comparison of enantiotopic OMe singlets, and to show both *trans* C(3)H and *cis* C(3)H NMR singlets at δ 1.1 and 0.8 ppm respectively in a 96 : 4 ratio. No proton absorption intensity at δ 5.55–5.35 was noted, implying complete deuteration at C(α). The synthetic product, then, was the mixture of isomers **9**, **10**, **11**, **12** in the respective proportions 92.2 : 3.8 : 3.8 : 0.2. The OMe singlet in the presence of Eu(hfbc)$_3$ at higher field was the most intense (*cf* assignment in Fig. 3).

Synthesis of (2*S*,3*S*) - 2 - methoxymethyl - 2,3 - dideuterio - 1 - (dideuteriomethylene)cyclopropane by the same route led to product that was found to be 93% optically pure but only 87 : 13 (**10**+**12**): (**9**+**11**). The more downfield of the two enantiotopic C(3)H resonances for **10** and **12** in the presence of Eu(hfbc)$_3$ predominated (*cf* Fig. 3).

Trial kinetic runs at 198.8° with labeled substrates and with 2 - methoxymethyl - 1 - methylenecyclopropane **24** showed that [1,3]-carbon shifts of C(2) were approximately fivefold faster than the migration of C(3) to give (methoxymethyl)methylenecyclopropane **30**, a nondegenerate isomerization product readily separated from the 2-methoxymethyl isomers by chromatography. At low conversions, this process could be viewed as an irreversible competitive reaction and ignored in the kinetic analysis. In the kinetic run described below, the tetradeuterio (methoxymethyl) methylenecyclopropanes amounted to less than 5% of the pyrolysis reaction mixture.



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Pyrolysis of the best synthetic substrate, the (2*S*,3*R*) *trans* material (largely **9**) for 300 min. at 198.8° in the gas phase led to a mixture of the eight isomers **9–16**. Analysis of this mixture was accomplished in stages.

First, NMR integration of the proton singlets characteristic of each pair of enantiomers showed *trans* (**9**+**11**) : *cis* (**10**+**12**) : *anti* (**13**+**15**) : *syn* (**14**+**16**) isomers present in the proportions 56 : 20 : 17 : 7.

Second, in the presence of the chiral shift reagent Eu(hfbc)$_3$, *syn* and *anti* C(α)H protons were resolved into the distinct enantiopic forms: in the pyrolysis sample, one enantiomer of the pair **13**, **15** and one of the pair **14**, **16** was much more prominent than the other (Fig. 4).

Chemical precedent,[6,7] a precedent without exception to date, indicates that the [1,3]-shift in methylenecyclopropanes occurs with predominant inversion at the migrating carbon C(2) and with both rotatory modes at the non-pivot ring carbon C(3), as in the reactions **1**→**3**

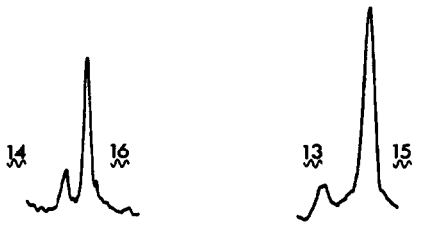


Fig. 4. Enantiotopically distinct vinyl proton absorptions in the presence of Eu(hfbc)$_3$; pyrolysis sample from substrate **9**, time-averaged spectra, several hundred transients.

and **1**→**5**.[6] From this precedent, the predominant enantiomers of *anti* and *syn* products from the [1,3]-sigmatropic isomerization of substrate **9** may be assigned as isomers **15** and **16**. The NMR integral ratios were **13** : **15** = 3 : 22 and **14** : **16** = 1 : 4, and the calculated mol percents then were deduced to be **13** = 2.3, **14** = 1.4, **15** = 14.7, **16** = 5.6.

Third, the C(3) protons *cis* to the methoxymethyl group were separated by the Eu(hfbc)$_3$ shift reagent: the relative intensities (2*S*,3*S*): (2*R*,3*R*), or **10** : **12**, were 69 : 31, and hence [**10**] = 13.8 and [**12**] = 6.2 mol percent.

Fourth, resolution of the enantiotopic OMe singlets with added Eu(hfbc)$_3$ indicated (2*S* : 2*R*) = [**9** + **10** + **13** + **14**] : [**11** + **12** + **15** + **16**] = 68 : 32, from which one may calculate [**9**] = 50.7 and [**11**] = 5.3.

From the NMR defined mol percents of the four pairs of enantiomers after 300 min. at 198.8°, kinetic Scheme II may be used to derive values for three combinations of rate constants. This scheme does not include a rate constant for direct interconversion of **13** + **15** with **14** + **16**: the system may be modeled well without doing so when starting from **9**, and, for present purposes, this process may be neglected.

For the overall isomerization [*trans* + *cis*]⇌[*anti* + *syn*] one calculates $(k_{13} + k'_{13}) = 1.82 \times 10^{-5}$ sec^{-1}. The isomerizations of Scheme II may be described by two homogeneous linear differential equations:[29]

$$\frac{-dx}{dt} = (2k_2 + 2k_3 + k_{13} + k'_{13})x + (k_{13} - k'_{13})y$$

$$\frac{-dy}{dt} = (k_{13} - k'_{13})x + (k_{13} + k'_{13})y$$

where x = [*trans*–*cis*] and y = [*anti*–*syn*]. The integral solutions which fit the experimental data give $k_{13} = 1.46 \times 10^{-5}$ s^{-1}, $k'_{13} = 0.36 \times 10^{-5}$ s^{-1}, and $k_2 + k_3 = 1.69 \times 10^{-5}$ s^{-1}. For this methylenecyclopropane system, thermal epimerization of the starting isomer is quite competitive kinetically with [1,3]-carbon shifts.

From the optical activity of the starting material and the product (92 and 36% optically pure) one may infer $(k_2 + k_{23} + k_i + k'_i) = 2.61 \times 10^{-5}$ s^{-1}. With the assumption $k_i = k_{13}$ (i.e. k(**9**→**13**) = 0) and $k'_i = k'_{13}$ (i.e. k(**9**→**14**) = 0), there remains but one undetermined independent parameter; this assumption is based on the results of Fig. 4 and validated through calculation with fair accuracy of [**13**] and [**14**] and other mol percents in the product mixture. Arithmetic gives $(k_2 + k_{23}) = 0.79 \times 10^{-5}$ s^{-1}, and thus knowledge of either k_2, or k_3, or k_{23} gives the other two.

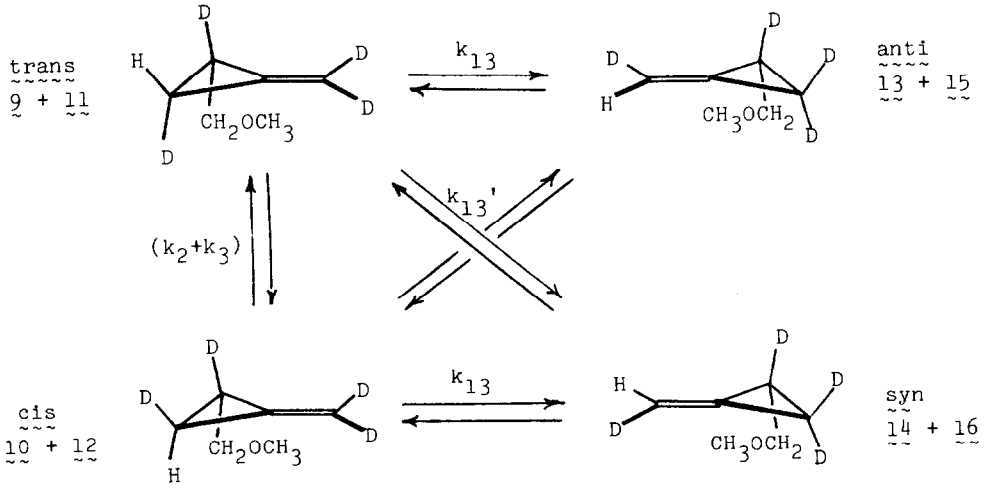
A satisfactory fit was found by varying one, deriving the others, and using the five non-zero rate constants to calculate the mol percents of isomers **9**–**16** as a function of time using a program based on the exact integral solution of the differential equations for the interconversions of isomers **9**–**16**.[30] The program accounted for the mol percents of eight isomers as a function of time with the thirty-two non-zero rate constants shown in Scheme III, yet it was used to find only one independent parameter.

The experimental findings and calculated mol percents, based on the rate constants (all × 10^{5}s) $k_i = 1.5$, $k'_i = 0.4$, $k_2 = 0.5$, $k_3 = 1.2$, $k_{23} = 0.3$ are summarized in Table 1. Included for comparison are values calculated with the parameters $k_i = 1.5$, $k'_i = 0.4$, $k_2 = 0.8$, $k_3 = 0.9$, and $k_{23} = 0$; neglect of the direct two-center epimerization process gives a distinctly poorer match between calculated and observed mol percents of isomers **9**–**12**.

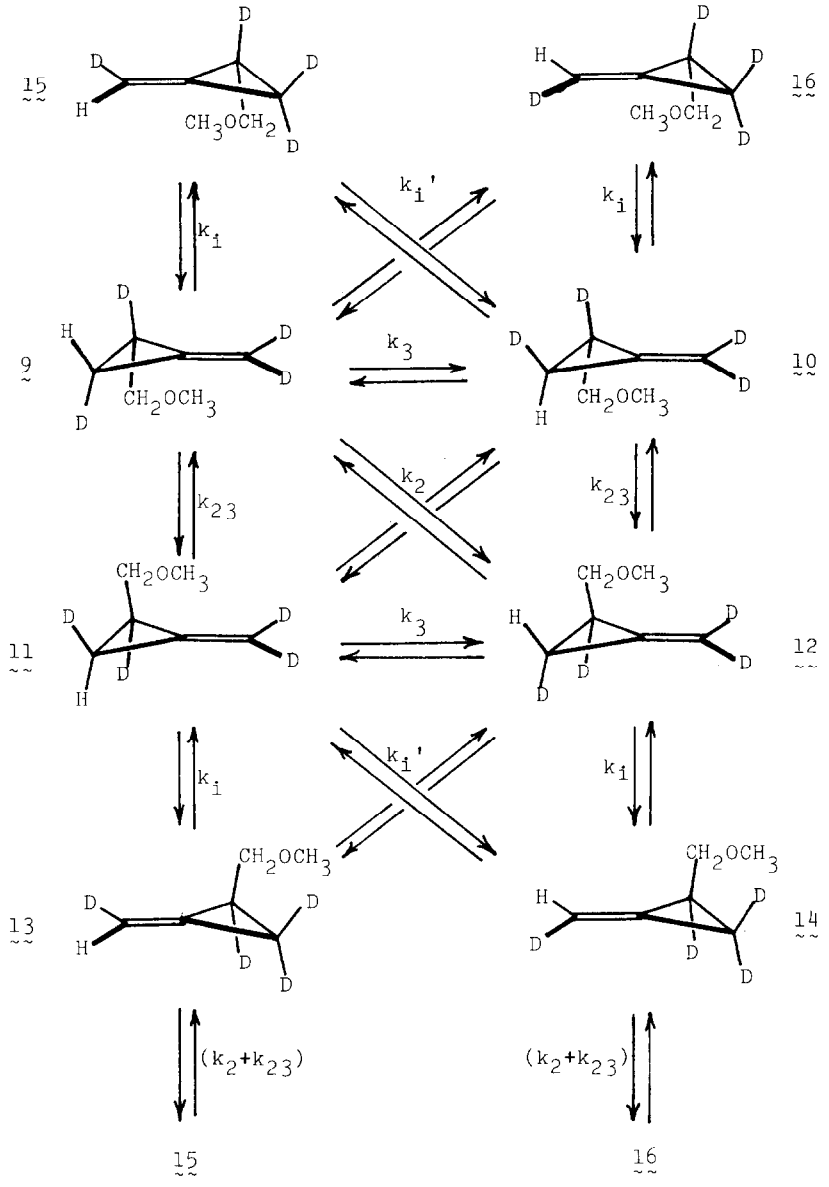
DISCUSSION AND CONCLUSIONS

The agreement between observed and calculated mol percents is well within the range of probable uncertainties in the experimentally determined values.

Thermal epimerizations described by k_2 and k_3 are of major importance, and k_{23}, though smaller, seems definitely larter than zero. The isomerization of **9** gives only **15** and **16** directly; the small amounts of **13** and **14** detected in the pyrolysis reaction mixture can be ascribed quantitatively to secondary reactions and to



Scheme II.



Scheme III.

isomeric impurities in the substrate **9**. This fact implies that *stereomutation at* C(2) *does not occur at the stage of a reactive intermediate along the reaction coordinate for* [1,3]*-carbon shifts.*

This experimental inference accords well with very recent calculations[31] predicting a rotational barrier separating **6** and **7** of 7 kcal/mol, a value significantly higher than the previous estimate, 1.8 kcal/mol.[12] A barrier of the order of 7 kcal/mol for rotation about the C(1)–C(pivot) bond should keep a perpendicular diradical intermediate from showing the **6⇄7** isomerization, for the barrier to ring closure is judged to be substantially lower, 3.3 kcal/mol.[12]

The C(3) deuteriomethylene group of **9** rotates preferentially clockwise; the C(3)–H *trans* to C(2)–CH_2OCH_3 in **9** rotates to become an *anti* C(α)–H in product **15** more often than it rotates counterclockwise to give a *syn* C(α)–H in product **16**: $k(9 \rightarrow 15)/k(9 \rightarrow 16) = k_i/k_i' = 4$. This stereoselectivity follows the pattern established by earlier work with Feist's ester[6] and *trans* - 2,3 - dimethyl - 1 - methylenecyclopropane,[7] compounds which isomerize thermally to give *anti* : *syn* [1,3]-carbon shift products in 3.7 : 1 and 6 : 1 ratios. The present stereochemical finding cannot be rationalized, as the earlier examples might have been, in terms of steric interactions of the C(3) *trans* substituent. Some more fundamental cause must be operative.[32]

The magnitude of the observed stereomutation at C(3) is consistent with perpendicular diradical intermediates **31** and **32**, and it implicates one or more additional stereomutation processes as well. Intermediate **31** might be formed from **9** by enlarging the C(2)C(1)C(3) angle and rotating the deuteriomethylene group at C(3) clockwise; intermediate **32** could be reached from **9** through the same angle opening and a counterclockwise rotation of the deuteriomethylene function. The intermediates would lead to [1,3]-shift products **15** and **16**, respectively.

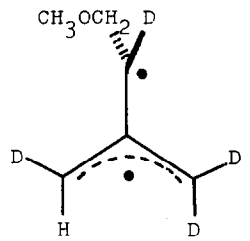
Intermediates **31** and **32** would be formed from isomer **9** in mol fractions *a* and *b*, with $a/b = k_i/k_i'$; from these intermediates would be formed [1,3]shift products half of

Table 1. Observed and calculated mol per cents of tetradeuterio-2-methoxymethyl(methylene)cyclopropane isomers 9–16

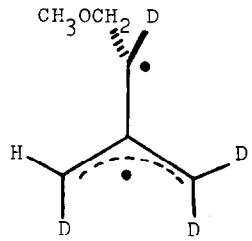
Isomers	t = 0	t = 300 min		
		obs	calcd[a]	calcd[b]
9	92.2	50.7	49.8	51.9
10	3.8	13.8	13.8	11.6
11	3.8	5.3	5.9	3.8
12	0.2	6.2	5.7	7.9
13	0	2.3	1.8	2.0
14	0	1.4	2.0	1.8
15	0	14.7	14.5	14.8
16	0	5.6	6.4	6.2

[a] Rate constants (cf. Scheme III) $k_1 = 1.5$, $k_1' = 0.4$, $k_2 = 0.5$, $k_3 = 1.2$, and $k_{23} = 0.3$, all times 10^{-5} s^{-1}; rate constants (cf. text) k_r, k_r', k_{sa}, and k_{sa}' = 0.

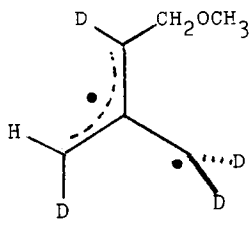
[b] Change of rate constants for epimerizations to $k_2 = 0.8$, $k_3 = 0.9$, and $k_{23} = 0$.



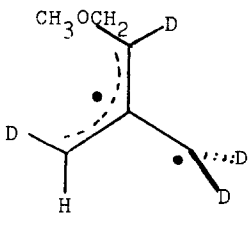
31



32



33

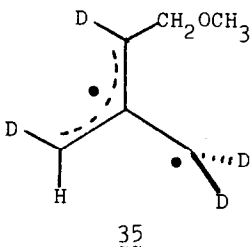


34

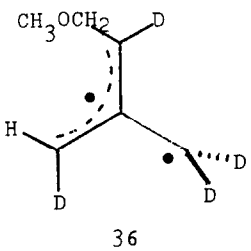
the time in the ratio a/b, starting material **9** $0.5(a^2+b^2)$ of the time, and the C(3) epimer **10** ab of the time. Thus the rate constant for epimerization at C(3) resulting from partitioning of intermediates **31** and **32** would be $k_3 = 2(k_i k_i')/(k_i + k_i')$. From the experimental values of k_i and k_i', k_3 (via **31** and **32**) $= 0.63 \times 10^{-5}$ s^{-1}. The observed value of k_3 is 1.2×10^{-5} s^{-1}; more direct epimerization at C(3) than required by intermediates **31** and **32** is observed, and hence another process (or other processes) must be contributing to the total k_3 observed.

How can this additional component of k_3 and the thermal epimerization corresponding to k_2 and k_{23} be explained? Though such thermal epimerizations have been known for some time, there seems to be no consensus as to how they take place. One possibility for the two-center epimerization would hypothesize rotation at C(2) and C(3) simultaneously, with a synchronous rotation at C(α) to make it locus of the isolated methylene group;[11] the disrotatory version of this model would generate intermediates **33** and **34**. Such intermediates lack a symmetry relationship between C(α) and C(3), and thus could give epimerization at C(2) and C(3) simultaneously without being diverted to [1,3]-shift products with partial retention at the pivot carbon.

If the ring-opening and ring-closing events were not limited to a single stereochemical mode and could occur in both conrotatory and disrotatory fashions, then these intermediates and their isomers **35** and **36** could account for k_{23} and k_2, and for k_3 being greater than k_3 (via **31** and **32**).



35



36

Hypothetical intermediates **33–36** would also give rise to direct *syn–anti* interconversions without 1,3-shifts; processes such as **13**→**14** and **13**→**16** might occur and might be detected through stereochemical kinetic experiments starting with **13**. Lack of stereochemical label at C(α) in our substrate **9** precludes access to reliable estimates of these rate constants: they must be small, but they could well be significantly larger than zero.

Microscopic reversibility enables one to deduce the stereochemistry of utilization of a C(α)HD group during [1,3]-carbon shifts even though suprafacial or antarafacial stereochemistry with respect to the allylic unit during 1,3-carbon shifts may not be derived uniquely. Neglecting stereochemically differentiated secondary deuterium isotope effects, $k(9\rightarrow10) = k(10\rightarrow9) = k_3$ (Scheme III), and $k(9\rightarrow10)k(10\rightarrow16)k(16\rightarrow9) = k(9\rightarrow16)k(16\rightarrow10)k(10\rightarrow9)$; hence $k(10\rightarrow16)k(16\rightarrow9) = k(9\rightarrow16)k(16\rightarrow10)$. Since it is also true that $k(10\rightarrow16) + k(9\rightarrow16) = k(16\rightarrow9) + k(16\rightarrow10)$, it follows that $k(9\rightarrow16) = k(16\rightarrow9)$ and $k(10\rightarrow16) = k(16\rightarrow10)$.

One may have, then, exclusive suprafacial utilization of the allylic unit, in the two specific senses defined by k_i and k_i', or as little as 58% suprafacial stereochemistry; the antarafacial transfer of the pivot carbon could be as great as $((2\times k_i')\times 100)/(k_i + k_i') = 42\%$ if every k_i' route to the perpendicular diradical intermediate were associated with a k_i stereochemistry of methylenecyclopropane formation, and *vice versa*.

The inversion–antarafacial stereochemistry for the [1,3]-shift in methylenecyclopropanes is "forbidden", according to orbital symmetry theory, and calculations[33] suggest it is of much higher energy than the inversion–suprafacial alternative. The present experimental results are consistent with suprafacial inversion being the exclusive stereochemical path and, in the absence of conflicting evidence, may be presumed to obtain. The presumption may be and should be tested; but there seem no grounds for anticipating an antarafacial–inversion stereochemical component in these isomerizations.

The experimental work of this paper should be extended in other ways. The assignments of enantiotopic vinyl protons in isomers **13–16** should be verified rigorously, and kinetic work starting from one of the isomers **13–16** should be done to probe for $k(13\rightarrow14)$ and $k(13\rightarrow16)$. Secondary deuterium kinetic isotope effects on methylenecyclopropane isomerizations will probably prove substantial and illuminating.[11,15] With additional stereochemical and kinetic work on this and other methylenecyclopropane systems, and further theoretical effects to understand both thermal epimerizations at ring carbons and [1,3]-carbon migrations, the mechanistic enigmas posed by the thermal isomerizations of methylenecyclopropanes may yet be resolved.

EXPERIMENTAL

General. All NMR spectra were taken on Varian XL-100 or HA-100 spectrometers. Mass spectra were taken on a CEC110-21B instrument by Dr. Richard Wielesek. Analytical GLPC on Perkin–Elmer F-11 or Varian 1520 gas chromatographs was done using 0.6-m × 3-mm 25% Carbowax 20M on Chromosorb W (Column A) and 2-m × 3-mm 10% Carbowax 20M on Chromosorb G 100–120 mesh (column B) with an Autolab 6300 Digital Integrator. Preparative GLPC on Varian A90-P3 or Varian 1520 chromatographs was done with 6-mm i.d. columns loaded with Carbowax 20M on Chromosorb supports (C) or UCW 98 on Chromosorb P (D).

trans - 2 - *Carbomethoxycyclopropanecarboxylic acid* **18** was prepared from diethyl *trans*-1,2-cyclopropanedicarboxylate (Aldrich) through transesterification with MeOH followed by partial saponification of **17**.[16] The acidic fraction of the mixture was isolated and purified through bulb-to-bulb distillation at 0.2 mm from a bath at 95–110° to give **18** as a white, low-melting solid;[17] NMR ($CDCl_3$): 11.5–11.1 (broad s, 1.1H), 3.7 (s, 3H), 2.3–2.0 (m, 2H), 1.6–1.45 (m, 2H).

Methyl trans - 2 - *hydroxymethylcyclopropanecarboxylate* **20**. To ester **18** (13.97 g, 97 mmol) in dry THF (50 ml) under N_2 was added dropwise over 30 min borane-dimethyl sulfide (Aldrich; 10.5 ml, 115 mmol) with stirring and cooling in a cold-water bath.[19] The mixture was stirred overnight at 25°, then treated dropwise with dry MeOH (30 ml). The resultant mixture was stirred several min., then concentrated by rotary evaporation. The residual viscous oil was dissolved in MeOH (200 ml); the soln was stirred 15 min. and concentrated; repetition of this process gave a clear oil containing, according to NMR analysis, about 10% of starting material. A second treatment of this material in dry THF (35 ml) with borane-dimethyl sulfide (8.8 ml, 92 mmol) followed by the same workup gave **20** as a viscous oil (12.12 g, 98% crude yield); bulb-to-bulb distillation from a bath at 56–76° (.05–0.1 mm) gave the purified product in 88% yield; NMR ($CDCl_3$): 3.7–3.3 (s on m, 5H), 2.5–2.3 (broad s, 1H), 1.9–1.5 (m, 2H), 1.35–1.1 (m, 1H), 1.0–0.8 (m, 1H); mass spectrum: *m/e* 130 (M^+ for $C_6H_{10}O_3$), 129, 128, 127, 113, 112, 111 (base peak).

Methyl trans - 2 - *methoxymethylcyclopropanecarboxylate* **21**. A stirred, ice-bath cooled soln of **20** (11.87 g, 91 mmol) and MeI (118 g, 0.83 mol, 9.1 eq) in dry THF (150 ml) under N_2 was treated portionwise with NaH (5.25 g of a 50% mineral oil dispersion, freed of oil by pentane washings; 110 mmol) over 20 min. The stirred mixture was allowed to warm to 25° over 2 hr, then diluted with ether and filtered. The salts which precipitated were washed well with ether and removed by filtration. The combined filtrates were concentrated by distillation through a 1-m × 11-mm glass helix-packed column; the residue was diluted with ether and the ethereal soln was filtered to remove the last of the inorganic salts, dried over $MgSO_4$, filtrated, concentrated, and distilled through a short-path still head to give **21** as a clear mobile liquid, b.p. 74–79° (14–16 mm), 6.474 g (49%), greater than 98% pure by GLPC (Column B, 135°); NMR ($CDCl_3$): 3.65 (s, 3H), 3.5–3.1 (s on m, 5H), 1.8–1.4 (m, 2H), 1.3–1.1 (m, 1H), 1.0–0.75 (m, 1H); mass spectrum: *m/e* 144 (M^+ for $C_7H_{12}O_3$), 143, 129, 116, 115, 114 (base peak).

trans - 2 - *Hydroxymethyl* - 1 - *methoxymethylcyclopropane* **22**. Ester **21** (1.51 g, 10.4 mmol) in 20 ml ether was added to a stirred slurry of $LiAlH_4$ (0.37 g, 9.9 mmol) in ether (25 ml) at reflux. After 1 hr, normal workup[20] and distillation afforded 1.2 g (99%) of **22** as a clear oil, b.p. 90–92° (13–14 mm), homogeneous by GLPC analysis on Column B at 135°; NMR ($CDCl_3$): 3.6–3.0 (s on m, 7H), 2.5–2.3 (broad s, 1H), 1.1–0.8 (m, 2H), 0.6–.04 (m, 2H); mass spectrum: *m/e* 116 (M^+ for $C_6H_{12}O_2$), 98, 97, 85, 83, 75 (base peak).

trans - 2 - *Methoxymethyl* - 1 - *bromomethylcyclopropane* **23**. The ether–alcohol **22** (1.2 g, 10.4 mmol) in dry ether (25 ml) under N_2 at −78° was treated dropwise with PBr_3 (1.04 g, 3.8 mmol), then allowed to warm to 25° overnight.[21] Sat. $NaHCO_3$aq was added; the organic layer was separated and washed with water and brine, dried over $MgSO_4$, and filtered; the filtrate was concentrated and purified by bulb-to-bulb distillation (65–70°, 13–14 mm) to give **23** as a clear mobile liquid (1.52 g, 82% yield), greater than 95% pure according to GLPC analysis on Column D at 120°; NMR ($CDCl_3$): 3.5–3.1 (s on m, 7H), 1.2–1.0 (m, 2H), 0.9–0.6 (m, 2H); mass spectrum: *m/e* 180, 178 (M^+ for $C_6H_{11}BrO$), 149, 148, 147, 146, 139, 137 (base peak).

2 - *Methoxymethyl* - 1 - *methylenecyclopropane* **24**. Compound **23** (1.45 g, 8.1 mmol) was added by syringe in one portion to a stirred soln of dry sublimed t-BuOK (1.022 g, 9.1 mmol) in dry dimethyl sulfoxide (10 ml) under N_2. The resultant brown-colored mixture was stirred for 3 hr, then poured onto approximately 30 ml of sat.NH_4Claq. The mixture was heavily salted and extracted with ether (5 × 20 ml); the combined ether extracts were washed with water and sat. NaClaq, dried over $MgSO_4$, filtered, and concentrated by distillation through a 1-m × 11-mm glass helix-packed column. Preparative GLPC of the residue on Column C at 60° afforded 50 mg of pure 2 - methoxymethyl - 1 - methylenecyclopropane; NMR (C_6D_6): 5.55–5.35 (broad d, 2H), 3.3–3.1 (s on d, 5H), 1.8–1.5 (m, 1H), 1.3–1.0 (m, 1H), 0.9–0.7 (m, 1H); mass spectrum: *m/e* 98 (M^+ for $C_6H_{10}O$), 97, 74, 73, 68, 66, 59, 58 (base peak).

Ozonolysis of methyl trans-2-*phenylcyclopropanecarboxylate* **19**.[18] A stirred soln of **19** (9.0 g, 51 mmol) in EtOAc (300 ml) at 0°

was treated with O_3 from a Welsbach apparatus (110 V, 0.5 l/min. flow rate). After 11 hr, when less than 5% of the starting material remained as indicated by GLPC analysis on Column A at 150°, the O_3 stream was stopped, 20% H_2O_2aq (45 ml) was added, and the mixture was stirred at room temp. overnight. The organic layer was separated, the aqueous layer was extracted once with EtOAc, and the combined organic layers were treated with Pt black to decompose excess peroxide. Drying over $MgSO_4$, filtration, concentration, and bulb-to-bulb distillation from a bath at 75–110° (0.05–0.75 mm) afforded crude **18** as a syrupy oil (7.45 g). Reduction of part of this material (6.93 g) with borone-dimethyl sulfide (6.4 ml, 67.2 mmol) gave **20** (5.67 g); methylation as described above and distillation gave **21** (2.02 g; 29% yield from **19**) identical in all respects to the sample of **21** derived through synthesis starting from **17**.

α - Deuterio - trans - β - triphenylstannylstyrene.[25] Triphenyltin deuteride[34] (79 g, 0.224 mol) and phenylacetylene (28.05 g, 0.275 mol) were combined with mechanical stirring under N_2: the mixture, irradiated with a sun lamp, exhibited a vigorous exothermic reaction after a few min. The mixture cooled and solidified; after 24 hr it was pulverized and washed ten times with pentane to leave *α*-deuterio-*trans*-*β*-triphenylstannylstyrene as a white crystalline solid, m.p. 119–120° (lit[26] m.p. 119–20° for the unlabeled compound) in 65% yield.

α,β - Dideuterio - trans - β - triphenylstannylstyrene, m.p. 119–120°, was prepared in a similar fashion from triphenyltin deuteride[34] and phenylacetylene-d_1.[35]

cis-1,2-*Dideuteriostyrene.* A soln of *α*-deuterio-*trans*-*β*-triphenylstannylstyrene (61.5 g, 0.14 mol) in dry THF (20 ml) at −78° under N_2 was treated with n-BuLi (2.4 M in hexane, 100 ml, 0.16 mol) over 2 hr with stirring. The mixture was allowed to warm to 0°, chilled again to −78°, and quenched with 10 ml of O-deuterio-methanol.[36] The resultant suspension was diluted with pentane and filtered through a pad of Celite and $MgSO_4$; the pad was washed several times with pentane, and the combined organic layers were carefully concentrated by rotary evaporation. A small amount of hydroquinone was added, and the product was flash-distilled (bath temp. 80° (1–2 mm)) through a 150-mm Vigreux column and a short-path still head into a dry ice-cooled receiver. The distillate was *cis*-1,2-dideuteriostyrene contaimnated by small amounts of pentane and THF. The product (63% yield) was greater than 98% stereochemically pure as judged from the triplets in the NMR spectrum for *β*-proton at *δ* 5.8 (*cis*) and 5.3 (*trans*) *ppm.*

trans-1,2-*Dideuteriostyrene* of greater than 97% stereochemical integrity was prepared from phenylacetylene following the general procedures detailed above.

cis-β-Deuteriostyrene, prepared from phenylacetylene-d_1 and triphenyltin hydride, was obtained as an 82 : 18 mixture of *cis* : *trans* isomers. The lack of stereospecificity was subsequently ascribable to insufficient washing of the intermediate *β*-triphenylstannylstyrenes with pentane.

Methyl 2 - phenyl - trans - 2,3 - dideuteriocyclopropanecarboxylate.[37] A stirred soln of *trans*-1,2-dideuteriostyrene (11.17 g, 0.105 mol) and $CuSO_4$ (1.5 g, 0.009 mol) in cyclohexane (10 ml) heated in a 90°-bath was treated dropwise with a soln of ethyl diazoacetate (14.55 g, 0.128 mol) in cyclohexane (35 ml) over 7 hr under N_2. The mixture was allowed to cool to 25° and was diluted with ether; filtration through Celite and concentration afforded the crude ethyl 2 - phenyl - *trans* - 2,3 - dideuteriocyclopropanecarboxylates, which were converted to the corresponding methyl esters (abs MeOH, *p*-toluenesulfonic acid). Bulb-to-bulb distillation at 65–95° (0.05–0.1 mm) gave the methyl esters in 51% yield. A sample of the *trans* product (*dl*-**27** methyl ester) was isolated by preparative GLPC on Column C at 160°; NMR ($CDCl_3$): 7.4–7.0 (m, 5H), 3.7 (s, 3H), 1.95–1.8 (d, J = 5, 1H), 1.75–1.5 (d, J = 5, 1H).

trans - 2 - (*Dideuteriohydroxymethyl*) - trans - 2,3 - *dideuterio* - 1 - *methoxymethylcyclopropane.* The racemic 2 - phenyl - *trans* - 2,3 - dideuteriocyclopropanecarboxylates were equilibrated with NaOMe (1.9 g, 35 mmol) in dry DMSO (50 ml) at 25° under N_2 overnight to give a 19 : 1 mixture of *trans* : *cis* isomers. Ozonolysis, borane-dimethyl sulfide reduction, methylation, reduction with $LiAlD_4$, and vacuum distillation gave the tetradeuterio alcohol (0.87 g); NMR ($CDCl_3$): 3.4 (s on m, 5H), 3.4–3.1 (broad s, 1H), 1.0–0.8 (broad d, J = 5, 1H), 0.5–0.3 (broad d, J = 5, 1H).

trans - 2 - *Methoxymethyl* - trans - 2,3 - *dideuterio* - 1(*bromodideuteriomethyl*)*cyclopropane* was obtained (0.868 g, 82% yield) from the labeled cyclopropylcarbinol (0.78 g) by treatment with PBr_3 in ether at −78°; NMR ($CDCl_3$): 3.3 (s, 5H), 1.3–1.1 (m, 1H), 0.7–0.5 (m, 1H).

2 - *Methoxymethyl* - trans - 2,3 - *dideuterio* - 1 - *dideuteriomethylenecyclopropane* was prepared from the bromide (0.845 g) by treatment with t-BuOK in DMSO as described above; the product, after purification by preparative GLPC on Column C at 60°, amounted to 50 mg; NMR (C_6D_6): 3.1 (s on d, 5H), 1.1 (broad s, 1H).

2 - *Methoxymethyl* - cis - 2,3 - *dideuterio* - 1 - *dideuteriomethylenecyclopropane* was prepared from *cis*-1,2-dideuteriostyrene by way of the seven-step sequence of reactions described above; NMR (C_6D_6): 3.1 (5H), 0.8 (broad s, 1H).

2 - *Methoxymethyl* - cis - 3 - *deuterio* - 1 - *methylenecyclopropane* was obtained from *β*-deuteriostyrene (82 : 18 *cis* : *trans*) and ethyl diazoacetate, according to the procedures detailed above. In C_6D_6 solution, the chiral shift reagent Eu(hfbc)$_3$ served to differentiate enantiotopic *syn* and enantiotopic *anti* C(*α*)–H resonances (Fig. 2).

Chiral copper catalyst **29** was prepared following the precedent of Aratani *et al.*[27] Bromination of *p*-t-butylphenol gave 2-bromo-4-t-butylphenol,[38] which was alkylated with 1-bromoheptane in acetone at reflux.[39] The Grignard reagent prepared from 2-bromo-4-t-butylphenyl heptyl ether was combined with D-alanine methyl ester hydrochloride[40] to give (*R*) - 2 - amino - 1,1 - di(5 - t - butyl - 2 - heptyloxyphenyl) - 1 - propanol, which was condensed with salicylaldehyde in benzene in the presence of *p*-toluenesulfonic acid. The salicylaldimine, a viscous dark-red oil, was added as an EtOH soln to a stirred slurry of cupric acetate monohydrate (1 eq.) in EtOH. The dark blue–green mixture was treated with 15% NaOHaq, concentrated under vacuum, diluted with water, and extracted with hexane. The combined organic extracts were dried ($MgSO_4$), filtered, and concentrated to give chiral catalyst **29** as a dark green mass, $[\alpha]_{546} + 594$ ($c = 2.5 \times 10^{-4}$, cyclohexane). It was used without purification in the condensations described below.

Reaction of menthyl diazoacetate with α,β-dideuteriostyrene in the presence of chiral copper catalyst **29**; (+)–(1S,2S,3S) *methyl* trans - 2 - *phenyl* - cis - 2,3 - *dideuteriocyclopropanecarboxylate.* In a typical reaction, *cis*-1,2-dideuteriostyrene (6.90 g, 65 mmol) in cyclohexane (20 ml) was combined with a cyclohexane soln of the optically active **29** (72 ml, 0.1 M soln, equivalent to 0.527 g, 0.72 mmol) under N_2 and treated dropwise with a soln of *dl*-menthyl diazoacetate[24] (16.13 g, 71.5 mmol) in cyclohexane (50 ml) over 11 hr with stirring and heating (bath temp. 80°). The cooled mixture was then filtered through Celite and concentrated under vacuum to a brown oil.

The products of two runs (from a total of 14.55 g dideuteriostyrene) were combined and bulb-to-bulb distilled at 85–105° (0.05–0.075 mm) to give a slightly yellow oil (29.98 g) shown by NMR integration of characteristic phenyl (7.4–7.0) and menthyl (5.0–4.6) resonances to consist of about 72% of *cis* and *trans* isomers of menthyl 2-phenyl-2,3-dideuteriocyclopropanecarboxylate and 28% of other menthyl esters. The mixture of esters was saponified with 30% NaOHaq (100 ml) in MeOH (100 ml) for 21 hr at reflux. A customary workup and treatment of the acidic material with diazomethane gave rise to 11.92 g of impure *trans* and *cis* methyl esters (4 : 1 ratio, by NMR analysis). This mixture was combined with the crude menthyl esters from another run (13.86 g), and the mixed esters were epimerized with NaOMe (2.53 g, 46 mmol) in DMSO (70 ml), then saponified to give impure *trans*-acid **28** (12.99 g). Resolution of this acid with quinine 25.5 g, 79 mmol) in 30 : 70 EtOH: hexanes [18] gave, as a first crop, 14.8 g of quinine salt. The salt was hydrolyzed in 125 ml of 10% HClaq; the acid obtained (4.70 g) was converted with diazomethane to the *trans* methyl ester. A sample purified by GLPC on Column C at 150° had an NMR spectrum identical with the spectrum obtained earlier for the racemic compound. In the presence of the chiral shift reagent Eu (Opt), only one OMe

singlet, the one appropriate to the (+)-(1*S*,2*S*) enantiomer, was observed under conditions known to give two well resolved signals for racemic or partially resolved methyl *trans*-2-phenylcyclopropanecarboxylate.

(+)-(1S,2S,3R) *Methyl* trans - 2 - *phenyl* - trans - 2,3 - *dideuteriocyclopropanecarboxylate* was prepared similarly, from *trans*-1,2-dideuteriostyrene (8.65 g, 81.5 mmol) and menthyl diazoacetate (27.1 g, 120 mmol) in the presence of chiral **29** (0.968 g, 1.3 mmol) in cyclohexane at 80°. Transformation of a small sample to the *trans* and *cis* methyl esters allowed analysis by NMR: the *trans* : *cis* ratio was 85 : 15. A sample of the *trans* isomer was purified by GLPC and shown to be 80% optically pure by NMR in the presence of Eu (Opt), the (+) isomer predominating. The bulk of crude menthyl ester product was epimerized, saponified and resolved with quinine as described above. Reaction with diazomethane gave the (+)-(1*S*,2*S*,3*R*) ester (3.72 g); a small sample purified by preparative GLPC and analyzed by NMR spectroscopy with the aid of Eu (Opt) as before showed the ester to be 100% optically pure. The NMR spectrum of this ester was identical to that of racemic ester obtained previously.

(2S,3R) - 2 - *Methoxymethyl* - 2,3 - *dideuterio* - 1 - (*dideuteriomethylene*)*cyclopropane* **9** was prepared from the (+)-(1*S*,2*S*,3*R*) *trans* - 2 - phenylcyclopropanecarboxylic acid **27** following the sequence of steps used for making racemic product from inactive deuterium-labeled acid. The product **9** was shown by NMR spectroscopy to have C(2)–C(3) deuterium atoms in 96 : 4 *trans* : *cis* stereochemical integrity. With the aid of Eu(hfbc)$_3$, the (2*S*) : (2*R*) enantiomeric ratio was shown to be 0.96 : 0.04; thus the sample was 92% optically pure.

(2S,3S) - 2 - *Methoxymethyl* - 2,3 - *dideuterio* - 1 - (*dideuteriomethylene*)*cyclopropane* **10** was made from the (+)-(1*S*,2*S*,3*S*) acid **28**; it was shown to have the C(2)–C(3) deuterium atoms in a *cis* : *trans* ratio of 87 : 13. There was also 0.06H at C(2) as evidenced by NMR spectroscopy. In the presence of optically active shift reagent, Eu(hfbc)$_3$, the enantiomeric methyl ether singlets in the NMR spectrum were differentiated, with the predominant (*S*) isomer giving rise to the upfield signal. The (2*S*) : (2*R*) enantiomeric ratio as evidenced by the average of eight integrations of the Me signals was 0.965 : 0.035: thus the (2*S*,3*S*) sample **10** was 93% optically pure. The C(3)–H proton, in the presence of Eu(hfbc)$_3$, showed a predominance of the downfield enantiomer (*cf* assignment in Fig. 3).

Gas-phase kinetics. Pyrolyses of the materials used in this study were done at 198.8° in a thermostatted 1-liter quartz flask heated by six 200-watt GE cartridge heaters. The temp. was controlled by a Bailey Instruments Model 253 Precision Temp. Controller and measured with a Hewlett Packard 2802A Digital Thermometer. The flask was connected, through a graded seal, to a vacuum system with greaseless Teflon stopcocks and Viton O-ring joints.[41]

The procedure consisted of expanding the substrate into the vacuum line (volume about 640 ml), then opening the stopcock to the evacuated, heated quartz flask and allowing the substrate to expand into it. When the pressure was equilibrated, the stopcock was closed and the time noted. Sample pressures were measured with a Baratron Type 170M-27A gauge. The sample was retrieved from the reactor by the reverse process; when the sample pressure in the vacuum line-static reactor system had equilibrated (about 10 sec), the sample was condensed into a liquid N_2-cooled cold-finger ampoule (volume about 20 ml). In this way, more than 90% of the sample was retrieved within 30 sec.

Pyrolysis of 2 - methoxymethyl - 1 - methylenecyclopropane gave a higher-retention-time component on Column B at 65°. A sample of the rearrangement product was isolated by preparative GLPC (Column C, 60°) and shown to have NMR spectral characteristics consistent with the structure of (methoxymethyl)methylenecyclopropane; NMR (C_6H_6): 6.3–6.1 (m, 1H), 4.3–4.1 (d of narrow m, 2H), 3.35 (s, 3H), 1.1–0.9 (narrow m, 4H).

Pyrolyses of **9** and other analogs of **24** were done in the same manner. The recovered pyrolysis samples were dissolved in C_6D_6; the solns were dried with molecular sieves (Type 4A, 8–12 mesh), then filtered through glass wool and analyzed by NMR spectroscopy. The 300-min. pyrolysis sample from **9** was analyzed and then treated with portions of the optically active shift reagent Eu(hfbc)$_3$, up to relative concentrations of shift reagent that differentiated the enantiomeric resonances of C(3) protons in **10** and **12** and of both *syn* and *anti* C(α)H resonances in racemic 2 - methoxymethyl - 3 - deuterio - 1 - methylenecyclopropane (Figs. 2–4). The analytical results are given in the text above.

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