

A. Tolman and R. B. King for their interest and gifts of ligands and Dr. D. L. Knirk for advice and the loan of a program.

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- (15) The expression was

$$\text{TCA} = \sum_{i=1}^4 C_i \left(1.0 - \frac{0.15}{(\tau - 7.0)} \right)^{i-1}$$

and the method of least squares gave (C_1 – C_4 = 116.7, 81.6, –310.9, and 465.4, respectively). Only symmetric ligands with TCA ≥ 118 were employed. TCA's given by Tolman were used except (1) for $(\text{C}_6\text{H}_5)_3\text{P}$, a value of TCA = 155⁹ was used and (2) for $(\text{-C}_3\text{H}_7\text{O})_3\text{P}$ a TCA = 122⁹.

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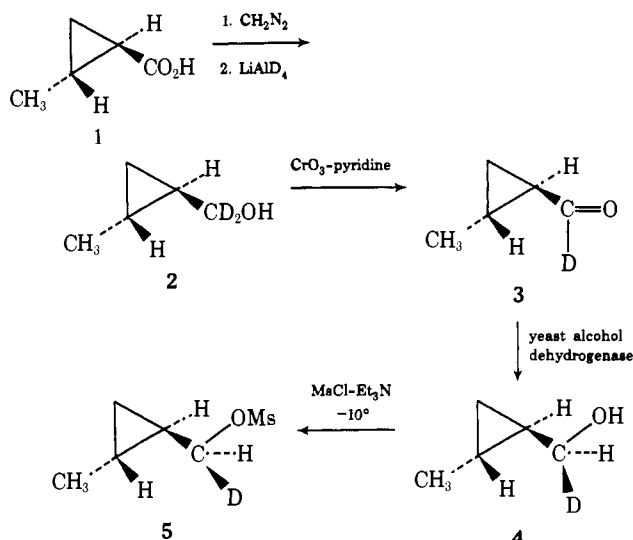
Received July 5, 1974

The (*trans*-2'-Methylcyclopropyl)methyl System. Stereochemistry of Ionization, Rearrangement, and Solvent Capture¹

Sir:

Acceptance of bisected structures for cyclopropylcarbinyl cations is based on a growing body of experimental² and theoretical work.^{2,3} However, except for molecular orbital calculations,³ all of the available evidence which strongly supports bisected cations was obtained with secondary and tertiary systems.² Recently Olah and coworkers⁴ challenged the concept that the parent cation (a primary system) is bisected and have proposed an unsymmetrically bridged structure on the basis of ¹³C chemical shift comparisons. Subsequently the use of ¹³C chemical shifts to decide between bisected and bridged structures was questioned,⁵ but there were still no direct experimental data to support a bi-

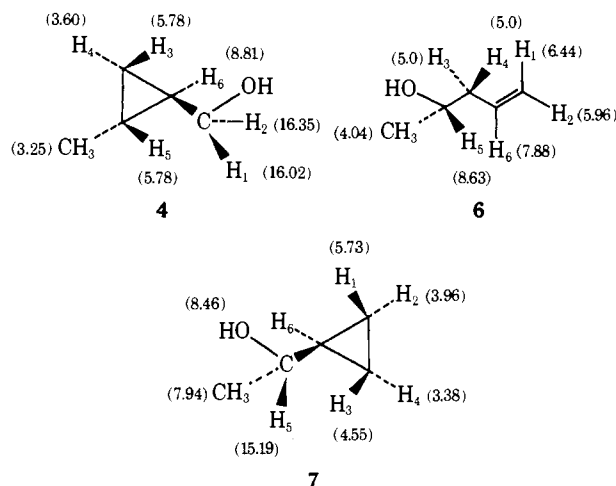
Scheme I



sected cation for primary cyclopropylcarbinyl systems. In this communication we present stereochemical evidence which bears on this important structural question.

Methanesulfonate **5** was prepared from optically active *trans*-2-methylcyclopropanecarboxylic acid by the sequence of reactions shown in Scheme I. Assuming that yeast alcohol dehydrogenase reduction of aldehyde **3** is stereospecific,⁶ the alcohol **7** used to prepare **5** was a mixture of diastereomers—77% 1*S*, 1'*R*, 2'*R* and 23% 1*S*, 1'*S*, 2'*S*.

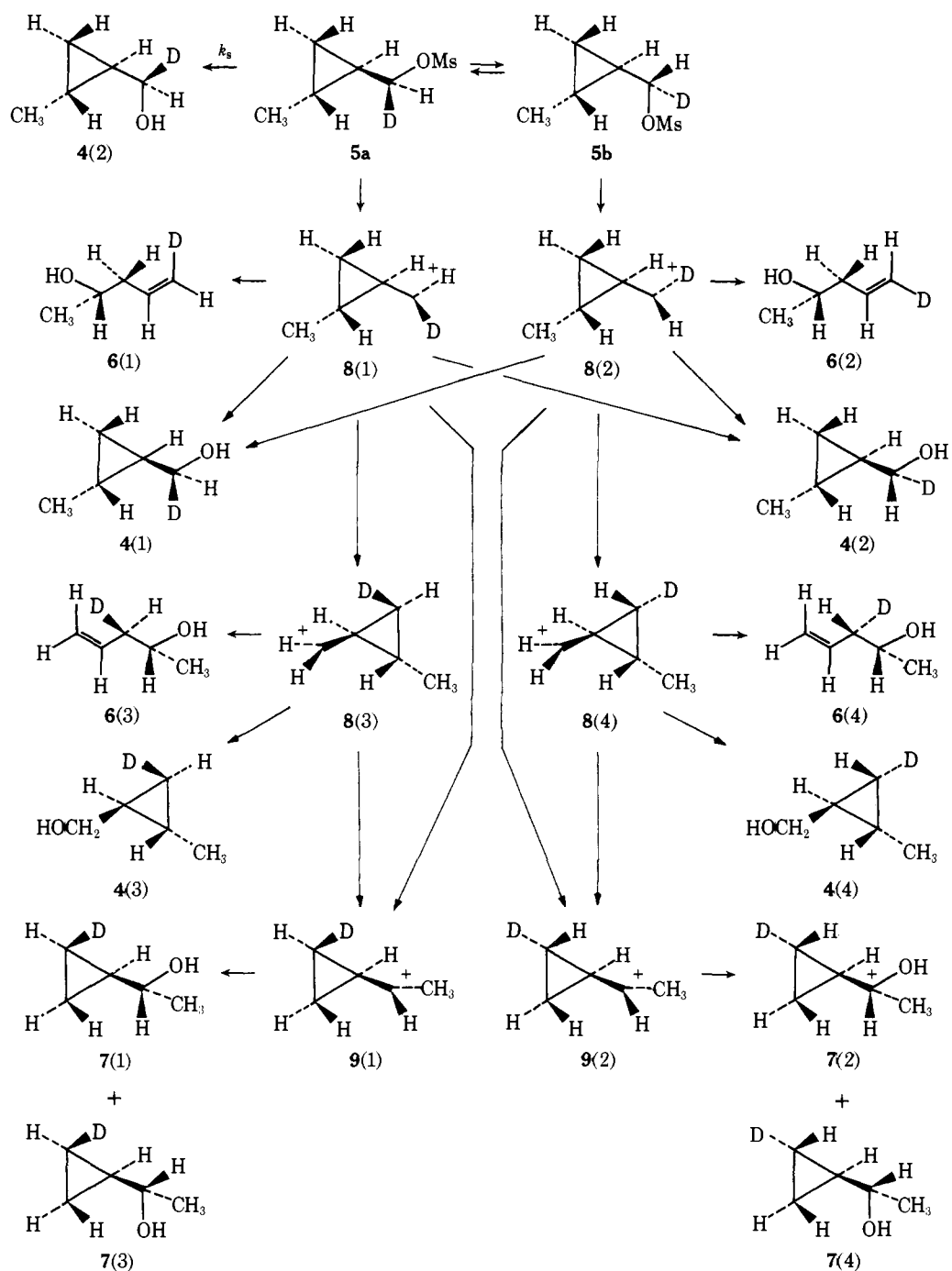
Hydrolysis of **5** (77% 1*S*, 1'*R*, 2'*R*) in 60% acetone-water with 2 equiv of γ -collidine, $k^{25^\circ} = (8.2 \pm 0.2) \times 10^{-2} \text{ sec}^{-1}$, gave three major products:⁸ **4** (26%), **6** (56%), and **7** (18%). The ²H distribution in each alcohol was deduced by measuring ¹H nmr intensities for samples where the chemical shifts of protons H₁–H₄ were separated as far as possible using Eu(fod)₃. Chemical shift assignments⁹ for **4** (0.235 mmol of Eu(fod)₃/0.413 mmol),¹⁰ **6** (0.076 mmol of Eu(fod)₃/0.384 mmol),¹¹ and **7** (0.118 mmol of Eu(fod)₃/0.257 mmol)¹² are summarized below. Although alcohols **4**,



6, and **7** are each inseparable mixtures of four ²H isomers, the mole fractions of ²H isomers for each skeletal isomer (²H at positions H₁–H₄) correspond directly to the ²H intensities listed in Table I.

An abbreviated mechanism is presented in Scheme II to account for the observed ²H distribution. Using the data in Table I,¹³ the stereochemistries of five individual steps—ionization of **5**, reaction of **8** with solvent at C₁, rearrangement of **8** to its enantiomer and to **9**, and reaction of **9** with

Scheme II



solvent at C₁—can be deduced.¹⁴ Our results are summarized by following the reactions initiated by ionization of mesylate **5** from conformer **5a**. Ionization is stereoselective with 74 ± 5% of the mesylate ionizing from conformer **5a** and the remainder from **5b**. Nucleophilic attack by water at C₁ of cation **8(1)** is also stereoselective, with 72 ± 7% going to **4(1)** and the remainder to **4(2)**.¹⁶ Cyclopropylcarbinyl-cyclopropylcarbinyl rearrangements **8(1)** → **8(3)** and **8(1)** → **9(1)** are stereoselective, 94 ± 8 and 84 ± 18%, respectively.¹⁷ The reaction of bisected cation **9(1)** with water at C₁ produces equal amounts of **7(1)** and **7(3)**, as expected.¹⁸ Complementary stereo- and regiochemical behavior was found for reactions initiated by ionization of **5** from conformer **5b**.

Replacing a hydrogen at C_{2'} by a methyl group enhances the solvolytic rate of **5** by 14.4 relative to the parent mesyl-

ate.¹⁹ By dissecting the rate enhancement for **5** into individual enhancements for conformers **5a** (10.9) and **5b** (3.5), it is obvious that both transition states are stabilized by the methyl group. The difference in rates is only a factor of 3.1, and could be attributed to electronic (slight preference for ionization from conformer **5a**^{6a}) or steric factors (slight buttressing which favors conformer **5a**). Obviously the electronic effect of an alkyl substituent at C_{2'} with regard to influencing the stereochemistry at C₁ during ionization or reaction with solvent is small and had been previously overestimated because of conformational and steric complications.²⁰ The lack of stereospecificity in some cyclopropylcarbinyl systems²¹ is now easily understandable.

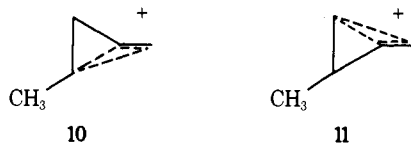
Finally, our data provide strong evidence for bisected cyclopropylcarbinyl cations as intermediates during solvolysis of primary systems. Sizeable rate enhancements for both

Table I. Relative ^1H and ^2H Intensities in 2-OH, 4-OH, and 5-OH

Compound		H ₁	H ₂	H ₃	H ₄
4 (before hydrolysis)	$^1\text{H}^a$	0.23	0.77		
	$^2\text{H}^b$	0.77	0.23		
	$^2\text{H}^c$	1.00			
4 (after hydrolysis)	$^1\text{H}^a$	0.60	0.67	0.84 ^d	0.89
	$^2\text{H}^b$	0.40	0.33	0.16	0.11
	$^2\text{H}^c$	0.43	0.30	0.18	0.09
6	$^1\text{H}^a$	0.53	0.76		1.71 ^e
	$^2\text{H}^b$	0.48	0.24		0.28
	$^2\text{H}^c$	0.57	0.15		0.28
7	$^1\text{H}^a$	0.68	0.82	0.68	0.82
	$^2\text{H}^b$	0.32	0.18	0.32	0.18
	$^2\text{H}^c$	0.37	0.13	0.37	0.13

^a All ^1H integrated intensities were obtained on a Varian XL-100-15 nmr spectrometer with an external ^{19}F lock. Each value represents the average of 20 integrations and was calculated on the basis $\sum_{n=1}^4 H_n = 3$. Average deviations ≤ 0.01 . ^b $^2\text{H} = 1 - ^1\text{H}$. ^c Corrected for 23% of the 1S, 1'S, 2'S diastereomer in starting mesylate. ^d Overlaps signal for H₃, total intensity at 1.84. ^e Not sufficiently separated to integrate individually.

conformers of **5** by the C₂' methyl group suggest interaction of the developing p orbital at C₁ with both adjacent cyclopropane bonds. In contrast, an unsymmetrically bridged bicyclobutonium structure²² implies interaction between C₁ and only one of the two adjacent cyclopropane bonds. One might have expected the methyl at C₂' to be more stabilizing than a factor of 3.1 for formation of **10** vs. **11**.²⁴ How-



ever, more compelling evidence for a bisected primary cyclopropylcarbanyl cation comes from comparisons of isotopic distributions in alcohols **4**, **6**, and **7**. Alcohol **4**(1) comprises 71% of **4**(1) + **4**(3) and **4**(2)¹⁵ comprises 77% of **4**(2) + **4**(4). In addition **4**(1) + **4**(2), **6**(1) + **6**(2), and **7**(1) + **7**(2) constitute 73, 72, and 74%, respectively, of alcohols **4**, **6**, and **7**. These similarities indicate that the distributions of ^2H isomers in each skeletal isomer only differ by a factor representative of the proportion of **5** which ionizes from each conformer. Bisected cations **8**(1) and **8**(2) should have nearly identical stereo- and regiochemistries for reaction with solvent and rearrangement in agreement with our findings, whereas bicyclobutonium ions **10** and **11** should not.

Supplementary Material Available. Reduction of the data will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for \$4.00 for photocopy or \$2.00 for microfiche, referring to code number JACS-74-7591.

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- The observed rotation for **4**, $[\alpha]^{30\text{D}} -26.0^\circ$ (*c* 0.85, CHCl_3), corresponds to 77% 1S, 1'R, 2'R and 23% 1S, 1'S, 2'S if one assumes that the deuterium at C₁ does not contribute to the observed rotation. An nmr spectrum of **4** with $\text{Eu}(\text{fod})_3$ shows clearly resolved diastereotopic protons at C₁ ($\Delta\delta$ up to 0.3 ppm). The two broad doublets of unequal intensity collapse to two singlets of unequal intensity, 0.77 ± 0.01 and 0.23 ± 0.01 protons, upon irradiation at the H₆ resonance frequency. The upfield signal results from hydrogen in the pro-R position of the 1S, 1'R, 2'R diastereomer, and the downfield signal, from hydrogen in the pro-R position of the 1S, 1'S, 2'S diastereomer.
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- $J_{1,2} = 11$ Hz, $J_{1,6} = J_{2,6} = 7$ Hz, $J_{3,4} = J_{4,5} = 4$ Hz, $J_{4,6} = 11$ Hz, $J_{5,\text{CH}_3} = 6$ Hz.
- $J_{1,6} = 17.6$ Hz, $J_{2,6} = 10.5$ Hz, $J_{3,5} = J_{4,5} = J_{5,\text{CH}_3} = 6.4$ Hz, $J_{3,6} = J_{4,6} = 7.3$ Hz.
- $J_{1,2} = 4.8$ Hz, $J_{1,3} = 9.4$ Hz, $J_{1,4} = 5.3$ Hz, $J_{1,6} = J_{3,6} = 4.8$ Hz, $J_{2,3} = 5.2$ Hz, $J_{2,4} = 8.8$ Hz, $J_{2,6} = J_{4,6} = J_{5,6} = 8.0$ Hz, $J_{3,4} = 4.2$ Hz, $J_{5,\text{CH}_3} = 6.0$ Hz.
- Reduction of the data will appear following these pages in the microfilm edition of this volume of the journal. See paragraph at end of paper regarding supplementary material.
- A detailed treatment of the data will be furnished in the full paper. Isotope effects should be small but may introduce small errors for comparisons between skeletal isomers or positional ^2H isomers.¹⁵
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- A careful analysis of the data suggests that a small amount of **4**(2) is formed from **5** by a k_3 process.
- The stereochemistries of the cyclopropylcarbanyl-cyclopropylcarbanyl rearrangements agree with previous work,² and a high degree of stereoselectivity is expected. The large uncertainty for **8**(1) \rightarrow **8**(2) arises because the concentrations of **4**(3) and **4**(4) cannot be determined with the same accuracy as those of **6**(1), **6**(2), **7**(1), and **7**(2).
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- The structure shown on p 151 (ref 4a), for a " $^{13}\text{C}_{2,4}$ -cyclopropylcarbonyl ion," is very similar to that used by Roberts²³ and coworkers (p 281, Figure 6) to describe a "bicyclobutonium ion."
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- Ionization of **5a** should give **10**, while ionization of **5b** should give **11**.
- University of Utah Research Fellow, 1971-1973.

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Received October 2, 1974

Structure of Hexameric Trimethylsilyllithium, a Folded Chair

Sir:

We wish to report the first crystal structure of a hexameric lithium derivative which provides a detailed picture of the lithium aggregate in $(\text{LiSiMe}_3)_6$ and also shows the participation of silicon in an electron deficient structure.[†] Two views of this structure are shown in Figure 1a and 1b. It is found that the trimethylsilyllithium framework can best be represented as a chair-form six-membered lithium ring of approximate D_{3d} symmetry with each face occupied by a bridging trimethylsilyl group. This is in contrast to the distorted octahedron with two open faces previously postulated for simple hexameric organolithium derivatives,¹ and to the hydrogen-bridged structure proposed by Craubner.² The 12 shortest lithium-lithium distances fall into two classes of six distances each. The shorter of these two classes averages 2.70 Å (av esd 0.03 Å) and occurs between the lithium atoms adjacent to one another on the edge of the ring. This distance is close to twice the covalent radius (1.23 Å) and is similar to the lithium-lithium bond distance (2.42-2.63 Å) observed in the methyl-³ and ethyllithium tetramers⁴ and to that recently reported in the dimeric bicy-