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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 (C_6H_5)₃P, a value of TCA = 155° was used and (2) for (*i*-C₃H₇O)₃P a TCA = 122°.

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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 biScheme 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 alcohol⁷ used to prepare 5 was a mixture of diastereomers-77% 1S, 1'R, 2'R and 23% 1S, 1'S, 2'S.

Hydrolysis of 5 (77% 1S, 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} 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 H_1-H_4 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 $Eu(fod)_3/0.384 \text{ mmol})$,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 2 H isomers. the mole fractions of ²H isomers for each skeletal isomer $(^{2}H \text{ at positions } H_{1}-H_{4})$ correspond directly to the ^{2}H 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 C_1 , rearrangement of 8 to its enantiomer and to 9, and reaction of 9 with Scheme II



solvent at C_1 —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 C_1 of cation 8(1) is also stereoselective, with 72 ± 7% going to 4(1) and the remainder to 4(2).¹⁶ Cyclopropylcarbinylcyclopropylcarbinyl 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 C_1 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 C_1 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)	${}^{1}H^{a}$	0.23	0.77		
	${}^{2}\mathbf{H}^{b}$	0.77	0.23		
	${}^{2}\mathrm{H}^{c}$	1.00			
4 (after hydrolysis)	¹ H ^a	0.60	0.67	0.84 ^d	0.89
	²H⁵	0.40	0.33	0.16	0.11
	${}^{2}\mathbf{H}^{c}$	0.43	0.30	0.18	0.09
6	¹Hª	0.53	0.76	1.71°	
	${}^{2}\mathrm{H}^{b}$	0.48	0.24	0.28	
	${}^{2}\mathbf{H}^{c}$	0.57	0.15	0.28	
7	${}^{1}\mathbf{H}^{a}$	0.68	0.82	0.68	0.82
	² H ^b	0.32	0.18	0.32	0.18
	${}^{2}\mathbf{H}^{c}$	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 ¹⁹F lock. Each value represents the average of 20 integrations and was calculated on the basis $\Sigma_{n=1}^4 H_n = 3$. Average deviations ≤ 0.01 . ^b ²H = 1 - ¹H. ^c Corrected for 23% of the 1S, 1'S, 2'S diastereomer in starting mesylate. ^d Overlaps signal for H₅, total intensity at 1.84. ^e Not sufficiently separated to integrate individually.

conformers of 5 by the $C_{2'}$ methyl group suggest interaction of the developing p orbital at C_1 with both adjacent cyclopropane bonds. In contrast, an unsymmetrically bridged bicyclobutonium structure²² implies interaction between C_1 and only one of the two adjacent cyclopropane bonds. One might have expected the methyl at $C_{2'}$ to be more stabilizing than à factor of 3.1 for formation of 10 vs. 11.24 How-



ever, more compelling evidence for a bisected primary cyclopropylcarbinyl 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) + 6(2)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, $24 \times$ 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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- $= J_{4,6} = 7.3 \text{ Hz}.$ (12) $J_{1,2} = 4.8 \text{ Hz}, J_{1,3} = 9.4 \text{ Hz}, J_{1,4} = 5.3 \text{ Hz}, J_{1,6} = J_{3,6} = 4.8 \text{ Hz},$
- $\begin{array}{l} J_{2,3} = 5.2 \ \text{Hz}, \ J_{2,4} = 8.8 \ \text{Hz}, \ J_{2,6} = J_{4,6} = J_{5,6} = 8.0 \ \text{Hz}, \ J_{3,4} = 4.2 \ \text{Hz}, \ J_{5,CH_0} = 6.0 \ \text{Hz}. \end{array}$ (13) 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.
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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 $(LiSiMe_3)_6$ 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-