

g, 0.81 mmol) as described for 10a. Attempts at recrystallization failed. After drying in vacuum (50 °C) there was obtained 0.24 g (0.72 mmol, 88% yield) of 11 as a white powder: mp dec; <sup>1</sup>H NMR (CD<sub>3</sub>CN) δ 1.24 (t, 6 H, CH<sub>2</sub>CH<sub>3</sub>), 3.21 (m, 4 H, CH<sub>2</sub>CH<sub>3</sub>), 4.39 (s, 3 H, NCH<sub>3</sub>), 8.01 (d + m, 3 H, pyr-H<sub>6</sub> + NH), 8.84 (d + s, 2 H, pyr H<sub>9</sub> + H<sub>2</sub>); <sup>13</sup>C NMR (CD<sub>3</sub>CN) δ 13.9 (q), 37.0 (t), 37.1 (t) 50.5 (q), 128.1 (d), 139.6 (s), 146.5 (d), 148.7 (s), 149.1 (d), 164.4 (s), 165.7 (s); UV (95% C<sub>2</sub>H<sub>5</sub>OH) λ<sub>max</sub> 272 (ε 3000), 205 (ε 6500).

**1-Methyl-3,5-bis(ethoxycarbonyl)pyridinium perchlorate (10e)** was obtained analogously to other pyridinium salts. Recrystallization from methanol-diethyl ether gave, starting from 2.24 mmol pyridine, 0.60 g (1.78 mmol, 80% yield) of white crystals of 10e: mp 138–140 °C; IR (KBr) 3080, 1725 cm<sup>-1</sup>; <sup>1</sup>H NMR (CD<sub>3</sub>CN) δ 1.42 (t, 6 H, CH<sub>2</sub>CH<sub>3</sub>) 4.47 (q + s, 7 H, CH<sub>2</sub>CH<sub>3</sub> + NCH<sub>3</sub>), 9.26 (s, broad, 1 H, pyr-H<sub>4</sub>), 9.39 (s, broad, 2 H, pyr-H<sub>2,6</sub>); <sup>13</sup>C NMR (CD<sub>3</sub>CN/CDCl<sub>3</sub>) δ 13.0 (q), 48.6 (q), 62.8 (t), 130.3 (s), 143.9 (d), 148.6 (d), 159.7 (s); UV (95% C<sub>2</sub>H<sub>5</sub>OH) λ<sub>max</sub> 352 (ε 3800), 271 (ε 9000), 210 nm (ε 13 500).

**1-Benzyl-3,5-bis((ethylamino)carbonyl)pyridinium Bromide (10c).** To a stirred solution of 0.5 g (2.26 mol) of the corresponding amide in 8 mL of ethanol was added 1.4 mL (2.0 g, 11.8 mmol) of benzyl bromide. The solution was stirred for 24 h, after which time a precipitate had formed. After slow addition of diethyl ether, this precipitate was filtered with suction and washed with cold ether. Recrystallization from ethanol-diethyl ether gave 0.57 g (1.5 mmol, 66% yield) of white crystals: mp 209–210.5 °C; IR (KBr) 3250, 2980, 1660 cm<sup>-1</sup>; <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 300 MHz) δ 1.16 (t, 6 H, CH<sub>2</sub>CH<sub>3</sub>), 3.35 (m, 4 H, CH<sub>2</sub>CH<sub>3</sub>), 6.03 (s, 2 H, CH<sub>2</sub>Ar), 7.5 (m, 5 H, C<sub>6</sub>H<sub>5</sub>), 9.34 (t, 2 H,

NH), 9.52 (t, 1 H, pyr-H<sub>4</sub>), 9.81 (d, 2 H, pyr-H<sub>2,6</sub>); <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>) δ 14.5 (q), 34.7 (t), 63.8 (t), 129.3 (d), 129.4 (d), 129.6 (d), 133.8 (s), 141.6 (d), 146.0 (d), 160.6 (s).

**1-Benzyl-3,5-bis((diethylamino)carbonyl)pyridinium bromide (10d)** was prepared from *N,N,N',N'*-tetraethyl-3,5-pyridinedicarboxamide (0.5 g, 1.8 mmol). Recrystallization from acetonitrile-diethyl ether gave 0.55 g (1.23 mmol, 68% yield) of 10d as white crystals: mp 165–167 °C; IR (KBr) 2970, 1630, 1445 cm<sup>-1</sup>; <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 300 MHz) δ 0.99 + 1.13 (2 t, 12 H, CH<sub>2</sub>CH<sub>3</sub>), 3.19 + 3.41 (2 q, 8 H, CH<sub>2</sub>CH<sub>3</sub>), 5.94 (s, 2 H, CH<sub>2</sub>Ar), 7.57 (m, 5 H, C<sub>6</sub>H<sub>5</sub>), 8.73 (s, 1 H, pyr-H<sub>4</sub>), and 9.56 (s, 2 H, pyr-H<sub>2,6</sub>); <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>) δ 12.7 (s), 39.3 (t), 43.2 (t), 63.6 (t), 29.3 (d), 129.9 (d), 133.9 (s), 137.3 (s), 140.4 (d), 142.9 (d), 163.1 (s).

**1-Methyl-2,5-bis((ethylamino)carbonyl)pyridinium Fluorosulfonate (12).** Methyl fluorosulfonate (1 mL) was added to a solution of *N,N'*-diethyl-2,5-pyridinedicarboxamide (0.25 g, 1.13 mmol) in 50 mL of dry CH<sub>2</sub>Cl<sub>2</sub>. The solution was stirred for 65 h with exclusion of moisture. After evaporation of the solvent, there was obtained an oil, which became solid after drying in vacuum at 50 °C. The yield of 12 was 0.38 g (11.3 mmol, 100% yield) as a white powder: mp 163–165.5 °C; <sup>1</sup>H NMR (CD<sub>3</sub>CN) δ 1.25 (t, 6 H, CH<sub>2</sub>CH<sub>3</sub>), 3.42 (m, 4 H, CH<sub>2</sub>CH<sub>3</sub>), 4.35 (s, 3 H, NCH<sub>3</sub>), 7.98 (d, 1 H, pyr-H<sub>3</sub>), 8.32 (m, 2 H, NH), 8.75 (d, 1 H, pyr-H<sub>4</sub>), 9.06 (s, 1 H, pyr-H<sub>6</sub>); <sup>13</sup>C NMR (CD<sub>3</sub>CN) δ 14.8 (q), 36.4 (t), 36.5 (t), 48.2 (q), 128.4 (d), 136.0 (s), 145.9 (d), 148.1 (d), 151.3 (s), 161.1 (s), 162.3 (s); UV (95% C<sub>2</sub>H<sub>5</sub>OH) λ<sub>max</sub> 275 (ε 11 000), 206 nm (ε 10 000).

Attempts to alkylate the pyridine using other methods failed to give significant amounts of the desired pyridinium salt.

## γ-Silicon Stabilization of Carbonium Ions in Solvolysis. 4. Solvolysis of *cis*- and *trans*-3-(Trimethylsilyl)cyclohexyl and -3-*tert*-Butylcyclohexyl *p*-Bromobenzenesulfonates<sup>1</sup>

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The solvolyses of *cis*- and *trans*-3-(trimethylsilyl)cyclohexyl and -3-*tert*-butylcyclohexyl *p*-bromobenzenesulfonates (1–4) have been examined in several ethanol- and trifluoroethanol-water solvent mixtures. The α- and β-deuterium kinetic isotope effects have been determined, and the products have been identified. The *cis*-silyl compound (1) solvolyzes with participation by bridging across the ring between the γ-carbon and the reaction center, promoted by the γ-trimethylsilyl group. Products of the solvolysis are mainly those of substitution with retention of configuration, but a significant fraction of bicyclo[3.1.0]hexane is also formed. The *trans*-silyl compound (2) undergoes rate-determining ionization without significant acceleration by the trimethylsilyl group but with substantial participation by the β-hydrogens. The solvolysis products are 3- and 4-(trimethylsilyl)cyclohexenes formed by 1,2-elimination and cyclohexene formed by Wagner-Meerwein rearrangement and subsequent loss of the trimethylsilyl group. The solvolyses of the carbon analogue compounds (3 and 4) involve rate-determining ionization to form an intimate ion pair, followed by elimination of β-hydrogens or reaction with nucleophile. 1,2-Elimination is the principal product-forming process.

The effects of silicon substituents on carbonium ion formation have been investigated previously by several authors.<sup>2–6</sup> Apeloig and Stanger examined the solvolyses

of 2-(trimethylsilyl)-2-adamantyl and 2-methyl-2-adamantyl *p*-nitrobenzoates in 80% acetone and 97% 2,2,2-trifluoroethanol solvents at 25 °C.<sup>2d</sup> They found that the solvolysis rates for the two compounds were very similar. On the basis of the results of ab initio calculations, they concluded that, relative to a methyl substituent, an α-trimethylsilyl substituent destabilizes the 2-adamantyl cation by several kcal/mol and retards the rate of solvolysis.

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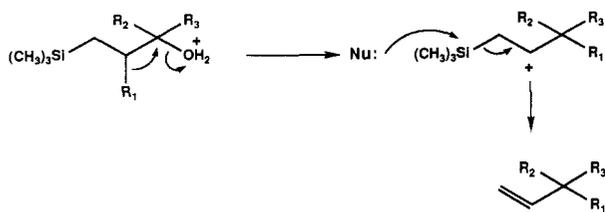


Figure 1. Silicon-controlled carbonium ion rearrangement.

By contrast, the presence of a  $\beta$ -silicon substituent strongly accelerates solvolysis.<sup>3-5</sup> Lambert et al. studied a series of substituted cyclohexyl trifluoroacetates that bore a  $\beta$ -trimethylsilyl substituent. When the  $\beta$ -trimethylsilyl and the leaving groups were *cis* to each other (*gauche* geometry), the compounds reacted 30 000–40 000 times faster than the unsubstituted parent cyclohexyl trifluoroacetate. By contrast, when the  $\beta$ -trimethylsilyl and the leaving groups were *trans* to each other (*antiperiplanar* geometry), the compounds were accelerated by factors as large as  $10^{12}$ . Lambert et al. concluded that in the *cis* compounds, the rate effects were approximately evenly distributed between inductive electron release and hyperconjugative stabilization by the 2-trimethylsilyl group. In the *trans* cases, hyperconjugative stabilization was vastly more important than inductive electron release. These authors estimated that the hyperconjugative effect was  $10^8$  times larger than the inductive effect, a conclusion consistent with earlier *ab initio* calculations on model systems by Jorgensen et al.<sup>7</sup> The observation by Fessenden et al. that *cis*- and *trans*-4-(trimethylsilyl)cyclohexyl *p*-toluenesulfonate solvolyze at rates that are comparable to the 4-*tert*-butyl analogues also indicates that the inductive effect of a silyl substituent is small.<sup>6</sup>

When silicon is located in the  $\gamma$ -position, a behavior different from the cases cited above is observed. Fleming and Patel found that a trimethylsilyl group placed in the  $\gamma$ -position could be used to control carbonium ion rearrangements.<sup>8</sup> In their work, a series of tertiary alcohols bearing a  $\gamma$ -trimethylsilyl group was treated with a boron trifluoride–acetic acid complex. The alkene products resulted from a Wagner–Meerwein rearrangement and loss of the trimethylsilyl group, with the nature of the rearrangement being a function of the  $\beta$ -substituent ( $R_1$ ); see Figure 1). When the  $\alpha$ -substituents ( $R_2$  and  $R_3$ ) were methyl or ethyl groups, hydrogen and phenyl migration were the predominant processes, but migration of  $R_1$  groups was less important for bulky  $R_2$  and  $R_3$  substituents. Fleming and Patel also found that reaction of 3-methyl-2-phenyl-4-(trimethylsilyl)-2-butanol gave a mixture of two rearranged alkenes, with hydrogen migration being favored over methyl migration. One might hypothesize that rearrangement of the initially formed carbonium ion yields a new cation which is stabilized by silicon. Attack by a nucleophile on the silicon atom, in a subsequent step, yields the alkene products. This form of Wagner–Meerwein rearrangement is described by the authors as a “silicon-controlled carbonium ion rearrangement”.

Fleming and Patel did not explore the generality of the silicon-controlled carbonium ion rearrangement, nor did they establish that carbonium ion intermediates were involved in the reactions examined. It is an interesting question whether the effect of silicon on the course of the reaction was exerted in the rate-controlling step or sub-

sequent to it as a product-partitioning effect (or both).

In the first report on solvolysis of  $\gamma$ -silicon-substituted alkyl sulfonates, Davis<sup>9</sup> found that 4-(trimethylsilyl)-2-butyl methanesulfonate reacted faster in acetic acid–water mixtures than did the 2-butyl analogue. However, he concluded that his experiments provided no evidence for silicon-stabilized ionic intermediates.

Our interest in these reactions relates to investigations that have been conducted in this laboratory on carbon and hydrogen participation in carbonium ion reactions. On the basis of the results reported by Fleming and Patel,<sup>8</sup> we expected that the  $\gamma$ -trimethylsilyl substituent might accelerate Wagner–Meerwein rearrangement. As a complement to earlier studies,<sup>10</sup> we decided to explore the possibility that a  $\gamma$ -trimethylsilyl group could promote neighboring alkyl or hydrogen participation in the solvolysis of secondary sulfonates. Simultaneously, we wished to examine the solvolysis of the analogous carbon compounds, where a  $\gamma$ -*tert*-butyl group replaces the trimethylsilyl group. The stereochemical requirements of any effects of  $\gamma$ -silicon substitution can be analyzed most easily in a conformationally stable ring system, such as in substituted cyclohexanes. The cyclohexane ring system, with a *tert*-butyl substituent used to maintain specific conformations, has been applied repeatedly to study the stereochemistry of organic reactions.<sup>11,12</sup> The classic work of Winstein and Holness showed that axial 3- and 4-*tert*-butylcyclohexyl *p*-toluenesulfonates solvolyzed approximately 3 times faster in acetic acid than did the corresponding equatorial isomers.<sup>11</sup> In general, it is observed that axial leaving groups are more reactive in solvolysis than are equatorial leaving groups.

Shiner and Jewett studied the solvolyses of isomeric *cis*- and *trans*-4-*tert*-butylcyclohexyl *p*-bromobenzenesulfonate.<sup>13-15</sup> With the *cis* isomer, they observed unusually large and noncumulative  $\beta$ -deuterium isotope effects for deuterium substitution in the axial positions. This result led them to conclude that solvolysis must be occurring with hydrogen participation in the formation of the carbonium ion.<sup>13,14</sup> For the *trans* isomer, the medium-sized, cumulative, axial,  $\beta$ -deuterium rate effects were used to conclude that solvolysis of this substance must be occurring through a twist-boat-like activated complex.<sup>15</sup>

We examined the solvolyses of *cis*- and *trans*-3-(trimethylsilyl)cyclohexyl *p*-bromobenzenesulfonate (1 and 2, respectively) and their  $\alpha$ -*d* and  $\beta$ -*d*<sub>4</sub> analogues in several ethanol and trifluoroethanol solvent mixtures. These results were compared with results obtained for the solvolyses of the analogous carbon compounds, *cis*- and *trans*-3-*tert*-butylcyclohexyl *p*-bromobenzenesulfonate (3 and 4, respectively), and their deuterated analogues. The results were also compared with those obtained earlier for the solvolyses of *trans*- and *cis*-4-*tert*-butylcyclohexyl *p*-bromobenzenesulfonate (5 and 6, respectively). The structures of these compounds are shown in Figure 2.

### Synthetic Method

3-(Trimethylsilyl)cyclohexanone was prepared from cyclohexenone and chlorotrimethylsilane in the presence of lithium, according to the method of Dunogues et al.<sup>16</sup>

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Table I. Rate Constants<sup>a</sup> for Solvolyses at 25 °C

	solvent <sup>b</sup>				
	80E	70E	60E	97T	70T
<i>cis</i> -3-(trimethylsilyl)cyclohexyl brosylate (1)	3.40 (0.01)	8.96 (0.09)		176.3 (0.80)	
<i>trans</i> -3-(trimethylsilyl)cyclohexyl brosylate (2)	0.89 (0.02)		3.2 (0.2)	1.99 (0.04)	4.13 (0.07)
<i>cis</i> -3- <i>tert</i> -butylcyclohexyl brosylate (3)	0.156 (0.002)			0.382 (0.004)	
<i>trans</i> -3- <i>tert</i> -butylcyclohexyl brosylate (4)	1.193 (0.004)			1.698 (0.008)	
<i>trans</i> -4- <i>tert</i> -butylcyclohexyl brosylate (5) <sup>c</sup>	0.22	0.51		0.39	0.99
<i>cis</i> -4- <i>tert</i> -butylcyclohexyl brosylate (6) <sup>c</sup>	1.26	2.68		1.64	5.05

<sup>a</sup> *k*'s are in units of 10<sup>-5</sup> s<sup>-1</sup>. All kinetic runs reported are the averages of several determinations. The errors in the rate constants are included in parentheses. <sup>b</sup> Solvents are as follows: 50E, 60E, 70E, and 80E represent 50, 60, 70, and 80 vol% ethanol, 50, 40, 30, and 20 vol% water, respectively; 70T and 97T represent 70 and 97 wt% 2,2,2-trifluoroethanol, 30 and 3 wt% water, respectively. <sup>c</sup> Reference 30.

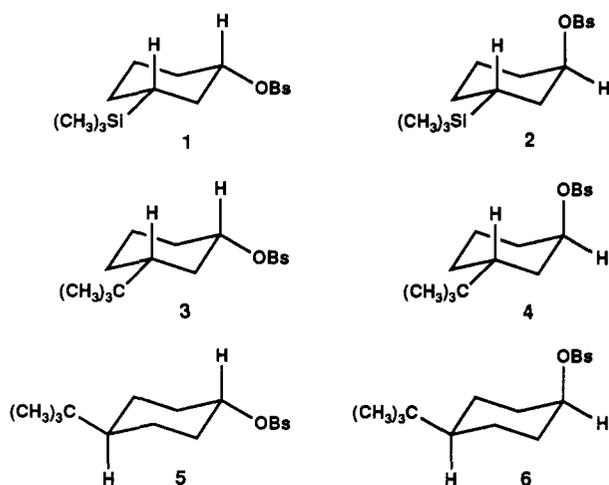


Figure 2. Isomeric 3- and 4-substituted cyclohexyl brosylates.

as modified by Wickham et al.<sup>17</sup> Reduction of the ketone to *cis*-3-(trimethylsilyl)cyclohexanol was accomplished with lithium aluminum hydride.<sup>6</sup> This reduction yields the *cis* isomer as the predominant product. *trans*-3-(Trimethylsilyl)cyclohexanol was obtained by reduction of the ketone with L-Selectride.<sup>18</sup> In each case, the pure *cis* or *trans* isomers were isolated by high-pressure liquid chromatography on a silica gel column using an ethyl acetate-hexane solvent mixture. 3-(Trimethylsilyl)cyclohexanone-2,2,6,6-*d*<sub>4</sub> was obtained by exchanging 3-(trimethylsilyl)cyclohexanone with deuterium oxide in the presence of sodium carbonate. The *cis* and *trans*  $\beta$ -*d*<sub>4</sub> alcohols were obtained from the  $\beta$ -*d*<sub>4</sub> ketone by the methods used for the undeuterated alcohols. Treatment of 3-(trimethylsilyl)cyclohexanone with diborane-*d*<sub>6</sub> afforded a mixture of *cis*- and *trans*-3-(trimethylsilyl)cyclohexanol-1-*d*.<sup>19</sup> The two isomers were separated by high-pressure liquid chromatography on a silica gel column using an ethyl acetate-hexane solvent mixture. The alcohols were converted to the corresponding *p*-bromobenzenesulfonates by a modification of the Tipson procedure.<sup>20</sup> The brosylates were also purified by high-pressure liquid chromatography on a silica gel column using an ethyl acetate-hexane solvent mixture. <sup>1</sup>H (360 and 60 MHz) NMR spectra were consistent with the assigned structures for all of the above compounds. Kinetic measurements were done conductometrically<sup>21</sup> using a

bipolar pulse conductance apparatus.<sup>22</sup>

The isomeric 3-(trimethylsilyl)cyclohexanols were converted to the corresponding *p*-bromobenzenesulfonates, where both sulfonyl oxygens were labeled with <sup>18</sup>O.<sup>23-27</sup> Spectroscopic analysis of the esters by NMR showed that no <sup>18</sup>O label had been incorporated into the bridging oxygen of the sulfonate esters.

A mixture of *cis*- and *trans*-3-*tert*-butylcyclohexanols was obtained from the catalytic hydrogenation of 3-*tert*-butylphenol, over a rhodium on alumina catalyst.<sup>28</sup> The mixture of alcohols was separated by high-pressure liquid chromatography on a silica gel column using an ethyl acetate-hexane solvent mixture. The mixture of alcohols was oxidized to 3-*tert*-butylcyclohexanone by using chromium trioxide in sulfuric acid.<sup>29</sup> 3-*tert*-Butylcyclohexanone-2,2,6,6-*d*<sub>4</sub> was prepared from the undeuterated ketone by exchange with deuterium oxide in the presence of sodium carbonate. The *cis* and *trans*  $\beta$ -*d*<sub>4</sub> alcohols were obtained from the  $\beta$ -*d*<sub>4</sub> ketone by reduction methods analogous to those used for the reduction of 3-(trimethylsilyl)cyclohexanone. *cis*- and *trans*-3-*tert*-butylcyclohexanol-1-*d* were prepared from 3-*tert*-butylcyclohexanone by reduction with lithium aluminum deuteride, which yields a mixture of isomers. The *cis* and *trans* isomers were separated by high-pressure liquid chromatography on a silica gel column using an ethyl acetate-hexane solvent mixture. The alcohols were converted to the corresponding *p*-bromobenzenesulfonates by a modification of the Tipson procedure.<sup>20</sup> The brosylates were also purified by high-pressure liquid chromatography on a silica gel column using an ethyl acetate-hexane solvent mixture. <sup>1</sup>H (360 and 60 MHz) NMR spectra were consistent with the assigned structures for all of the above compounds. Kinetic measurements on the 3-*tert*-butylcyclohexyl brosylates were also done conductometrically, as described previously.

The isomeric 3-*tert*-butylcyclohexanols were converted to the corresponding *p*-bromobenzenesulfonates, where both sulfonyl oxygens were labeled with <sup>18</sup>O.<sup>23-27</sup> Spectroscopic analysis of the esters by NMR showed that no <sup>18</sup>O label had been incorporated into the bridging oxygens of the sulfonate esters.

## Results and Discussion

The rate constants for the solvolyses of the isomeric 3-(trimethylsilyl)cyclohexyl brosylates and the 3-*tert*-bu-

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Table II. Isotope Effects<sup>a</sup> for Solvolyses of Substituted Cyclohexyl Brosylates at 25 °C

compd	eq substituent	OBs conf <sup>c</sup>	solvent <sup>b</sup>			
			80E	70E	50E	97T
1- $\alpha$ -d	<i>cis</i> -3-Me <sub>3</sub> Si	e	1.157	1.14		1.174
2- $\alpha$ -d	<i>trans</i> -3-Me <sub>3</sub> Si	a	1.20			1.17
5- $\alpha$ -d	<i>trans</i> -4- <i>tert</i> -Bu	e			1.17 <sup>d</sup>	
6- $\alpha$ -d	<i>cis</i> -4- <i>tert</i> -Bu	a			1.202 <sup>d</sup>	
1- $\beta$ -d <sub>4</sub>	<i>cis</i> -3-Me <sub>3</sub> Si	e	1.005	0.99		0.972
2- $\beta$ -d <sub>4</sub>	<i>trans</i> -3-Me <sub>3</sub> Si	a	2.80			2.86
3- $\beta$ -d <sub>4</sub>	<i>cis</i> -3- <i>tert</i> -Bu	e	1.988			2.058
4- $\beta$ -d <sub>4</sub>	<i>trans</i> -3- <i>tert</i> -Bu	a	2.697			3.002
5- $\beta$ -d <sub>4</sub>	<i>trans</i> -4- <i>tert</i> -Bu	e			2.425 <sup>d</sup>	
6- $\beta$ -d <sub>4</sub>	<i>cis</i> -4- <i>tert</i> -Bu	a			2.862 <sup>d</sup>	

<sup>a</sup>The errors for the isotope effects are all between 0.005 and 0.01. <sup>b</sup>Solvents are described in Table I. <sup>c</sup>Conformation in the most stable ground state; e = equatorial, a = axial. <sup>d</sup>These isotope effects were measured at 35 °C.<sup>14</sup>

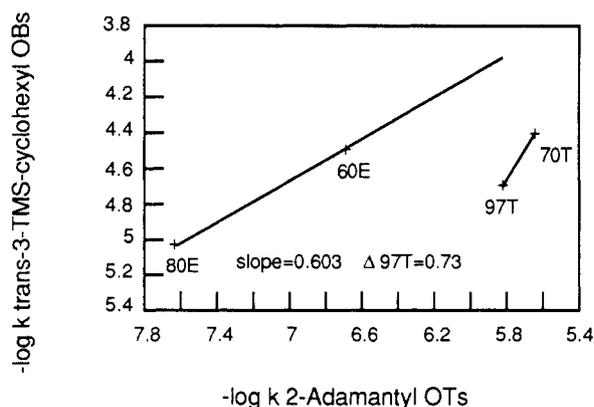


Figure 3. Ethanol-TFE plot for the solvolysis of *trans*-3-(trimethylsilyl)cyclohexyl brosylate.

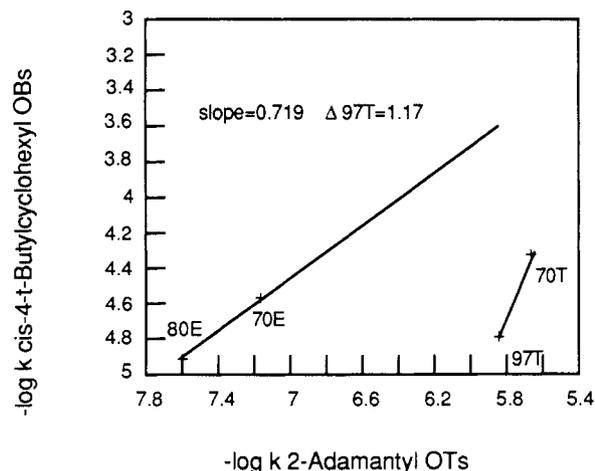


Figure 5. Ethanol-TFE plot for the solvolysis of *cis*-4-*tert*-butylcyclohexyl brosylate.

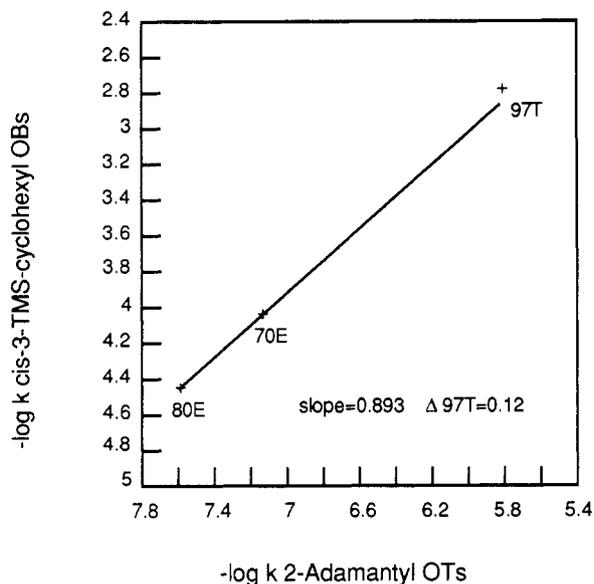


Figure 4. Ethanol-TFE plot for the solvolysis of *cis*-3-(trimethylsilyl)cyclohexyl brosylate.

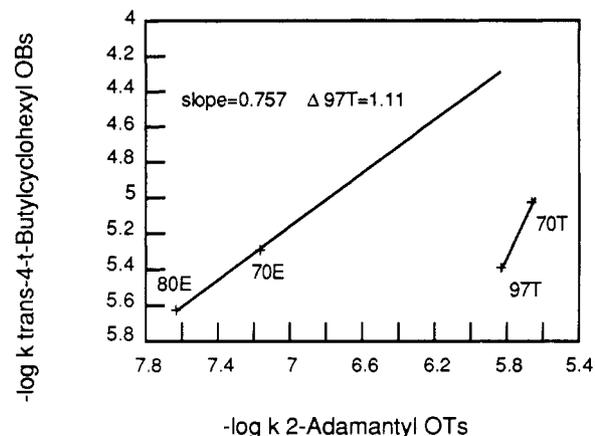


Figure 6. Ethanol-TFE plot for the solvolysis of *trans*-4-*tert*-butylcyclohexyl brosylate.

tylcyclohexyl brosylates in several solvents at 25 °C are listed in Table I, along with values for the 4-*tert*-butylcyclohexyl brosylates.<sup>30</sup> The observed isotope effects are listed in Table II. The ratios of products from the solvolysis reactions are given in Table III.

Ethanol-trifluoroethanol plots,<sup>31</sup> with use of the data from Table I, give (a) for compound 1, a linear correlation with slope 0.90, indicating a limiting solvolysis, and (b) for

compounds 2, 5, and 6 quite different plots with ethanol correlation lines showing a slope of about 0.6 and with the points for the trifluoroethanol (TFE) solvents lying considerably below these correlation lines. These plots suggest that the reaction mechanism for these compounds must be somewhat different from that for compound 1. Data for such plots for compounds 3 and 4 were not determined, owing to rather slow solvolysis rates, but it is assumed that they should be similar to those for compounds 5 and 6. The ethanol-trifluoroethanol plots are shown in Figures 3-6.

The isotope effects and rates for *trans*-3-(trimethylsilyl)cyclohexyl brosylate are very similar to those observed for *trans*-3-*tert*-butylcyclohexyl brosylate and for the 4-

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Table III. Product Yields in Solvolysis, 25 °C

product <sup>b</sup> formed by	solvent <sup>a</sup>				
	80E	70E	70T	97T	98H
(A) <i>cis</i> -3-(Trimethylsilyl)cyclohexyl Brosylate (1)					
1,3-elimination (bicyclohexane)	16%	18%	7%	8%	
substitution (retained config.)	84%	82%	93%	92% <sup>c</sup>	
ratio of ether to alcohol	0.7/1	0.4/1	0.6/1	11/1 <sup>c</sup>	
(B) <i>trans</i> -3-(Trimethylsilyl)cyclohexyl Brosylate (2)					
W-M rearrangement (cyclohexene)	16%	14%	44%	51%	59%
1,2-elimination (3- and 4-Me <sub>3</sub> Si-cyclohexenes)	? <sup>d</sup>	60%	42%	36%	30%
substitution (retained config.)	? <sup>d</sup>	18%	14%	13%	10%
(C) <i>cis</i> -3- <i>tert</i> -Butylcyclohexyl Brosylate (3)					
1,2-elimination (3- and 4- <i>t</i> -Bu-cyclohexene)	62%			81%	
substitution	38			19%	
(ratio of inversion to retention) <sup>e</sup>	40/1			3/1	
(D) <i>trans</i> -3- <i>tert</i> -Butylcyclohexyl Brosylate (4)					
1,2-elimination (3- and 4- <i>t</i> -Bu-cyclohexene)	82%			97% <sup>f</sup>	
substitution	18%			3% <sup>f</sup>	
(ratio of inversion to retention) <sup>e</sup>	7/1			0.8/1	

<sup>a</sup>Solvents are described in Table I. 98H is 98 wt % hexafluoroisopropyl alcohol-2 wt % water. <sup>b</sup>Relative abundance and identity of products were determined by <sup>2</sup>H NMR of reaction mixtures at 55 MHz. <sup>c</sup>Stereochemistry of substitution products and ether-to-alcohol ratio were confirmed by GC/MS. A small amount of trans ether, representing less than 4% of the total products, was also detected. <sup>d</sup>The relative percentages of elimination and substitution products could not be determined by <sup>2</sup>H NMR analysis in this reaction, owing to interference from solvent peaks in the spectrum. <sup>e</sup>Stereochemistry of substitution products for the 3-*tert*-butylcyclohexyl brosylate reactions was determined by HPLC of the alcohol products. <sup>f</sup>These values are approximate. By an alternative analysis the percent elimination could be as low as 83% and the percent substitution as high as 17%.

Table IV. Minimum Fraction Internal Return, 25 °C

compd	solvent <sup>a</sup>	
	80E	97T
<i>cis</i> -3-Me <sub>3</sub> Si-cyclohexyl OBs (1)	0.45 <sup>b</sup>	0.55
<i>trans</i> -3-Me <sub>3</sub> Si-cyclohexyl OBs (2)	0.07	0.08
<i>cis</i> -3- <i>t</i> -Bu-cyclohexyl OBs (3)	0.04	0.14
<i>trans</i> -3- <i>t</i> -Bu-cyclohexyl OBs (4)	0.00	0.08

<sup>a</sup>Solvents are described in Table I. <sup>b</sup>Reported as  $k_{eq}/(k_{eq} + k_t)$ .

*tert*-butyl analogue (see Tables I and II). The major product in TFE and hexafluoroisopropyl alcohol solvents in the case of the silicon compound, however, is cyclohexene formed by loss of the trimethylsilyl group after a Wagner-Meerwein rearrangement, a process similar to that reported by Fleming and Patel (see Table III).<sup>8</sup> The large  $\beta$ -*d*<sub>4</sub> isotope effect and the predominance of the cyclohexene product confirm that  $\beta$ -hydrogen participation occurs in the rate-determining step. Since there is very little or no rate acceleration, the  $\gamma$ -trimethylsilyl group does not promote participation but merely traps the carbonium ion subsequent to rearrangement. The likely explanation is that in any conformation in which the trans 2-hydrogen is antiperiplanar to the leaving group, as it must be to participate maximally, the trimethylsilyl group is gauche to the migrating bond, an orientation that allows for only minimal hyperconjugative stabilization of the developing vacancy at the  $\beta$ -carbon by the  $\gamma$ -carbon-silicon bond.<sup>7</sup>

The solvolysis of *trans*-3-(trimethylsilyl)cyclohexyl brosylate (2) where both sulfonyl oxygens were specifically labeled with <sup>18</sup>O was examined to estimate the degree of internal return that might be taking place. The results of the <sup>18</sup>O-scrambling experiments are presented in Table IV. For this compound, very little scrambling of the oxygen atoms occurred, suggesting either that internal return is significantly slower than solvolysis, as seems likely, or that significant internal return occurs without scrambling.<sup>25</sup> The very high  $\beta$ -deuterium isotope effects suggest that the carbonium ion intermediate is formed in the rate-determining step and that it is substantially stabilized by hyperconjugation, thus reducing the proportion of internal return. Very large  $\beta$ -isotope effects in cyclo-

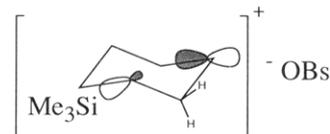


Figure 7. Silicon-promoted carbon-bridged carbonium ion.

hexyl systems with axial leaving groups have been observed previously and have been ascribed to a particularly favorable geometry for hyperconjugation between the developing p-orbital and the axial  $\beta$ -carbon-hydrogen bonds.<sup>13,14</sup>

The results for *cis*-3-(trimethylsilyl)cyclohexyl brosylate are quite different. The rate constants are larger than those observed for *cis*-3-*tert*-butylcyclohexyl brosylate or for the analogous 4-*tert*-butyl isomer, particularly in 97T (452 $\times$ ), and the  $\beta$ -*d*<sub>4</sub> isotope effects are much smaller (see Tables I and II). In the ethanolic solvents, no  $\beta$ -*d*<sub>4</sub> isotope effect is observed, and the effect in 97T is slightly inverse. The  $\alpha$ -*d* isotope effects are also smaller than expected. These results indicate that the reaction involves participation. The consistent formation of small yields of bicyclo[3.1.0]hexane suggest silicon-promoted carbon participation (see Table III).<sup>32</sup>

The solvolysis of *cis*-3-(trimethylsilyl)cyclohexyl brosylate, where the sulfonyl oxygens have been specifically labeled with <sup>18</sup>O, has also been examined, and the results are compiled in Table IV. Unlike the trans isomer, this compound shows substantial oxygen scrambling. It is proposed that substantial ion-pair recombination (internal return) must accompany the ionization of this substance. The silicon-bridged intermediate is capable of returning to starting material, reacting with a nucleophile to give substitution, or losing the trimethylsilyl group to form bicyclo[3.1.0]hexane. The silicon-promoted carbon bridge prevents backside attack by nucleophiles, thus accounting for the retention of configuration observed in the substitution products (see Figure 7).

(32) "Silicon-promoted carbon participation" is chosen to indicate bridging by the  $\gamma$ -carbon through the back lobe of the carbon-silicon bonding orbital.

The orientation of the two substituents in the transition state is approximately diequatorial rather than diaxial; in this conformation, all four  $\beta$ -C-H bonds have dihedral angles of  $60^\circ$  with the developing p-orbital vacancy, which allows for very little C-H hyperconjugative stabilization and gives small or inverse  $\beta$ - $d$  isotope effects. In the alternate, higher energy, 1,3-diaxial conformation<sup>33</sup> two of the  $\beta$ -C-H bonds would be antiperiplanar to the leaving group, favoring hyperconjugation, rearrangement,<sup>8</sup> and large  $\beta$ - $d_4$  effects, contrary to the observations. Thus, the silicon stabilizes the transition state, and presumably the carbonium ion intermediate, through a "W" conformation,<sup>34</sup> implicating the "percaudal"<sup>9</sup> interaction, which involves overlap of the reacting orbital on the  $\alpha$ -carbon with the back lobe of the carbon-silicon bonding orbital. Although earlier workers have speculated on this mode of carbonium ion stabilization, evidence confirming it was not obtained.<sup>35</sup>

Shiner et al. reported that a  $\gamma$ -silyl substituent promoted the solvolysis of 4-(trimethylsilyl)-2-butyl *p*-bromobenzenesulfonates.<sup>38</sup> They concluded that the  $\gamma$ -silyl group stabilized the intermediate carbonium ion through either the "W" or the "endo-sickle" conformations.<sup>34</sup> Davidson and Shiner reported the results of theoretical calculations on some  $\gamma$ -silicon-substituted model compounds.<sup>39</sup> They showed that silicon substitution stabilizes a cyclopropanoid bridged structure and is important in determining the properties of the carbonium ion. Thus,  $\gamma$ -silicon substitution does indeed appear to promote the formation of carbonium ions.

To provide a basis for comparison, the corresponding carbon analogues *cis*- and *trans*-3-*tert*-butylcyclohexyl *p*-bromobenzenesulfonate were also prepared and solvolyzed. The kinetic results did not reveal any unusual behavior in these compounds. The *trans* isomer (axial leaving group) was more reactive than the *cis* isomer (equatorial leaving group), as might be predicted (see Table I). Furthermore, the solvolysis rates for *trans*-3-*tert*-butylcyclohexyl *p*-bromobenzenesulfonate were very similar to the rates for *trans*-3-(trimethylsilyl)cyclohexyl *p*-bromobenzenesulfonate. The solvolysis rates for the 3-*tert*-butylcyclohexyl compounds were also very similar to the rates for the corresponding 4-*tert*-butylcyclohexyl isomers. The kinetic results, therefore, do not indicate that any special acceleration obtains in these reactions.

The  $\beta$ -isotope effects (see Table II) observed for the 3-*tert*-butylcyclohexyl systems do not follow the pattern observed for the analogous 3-(trimethylsilyl)cyclohexyl compounds. For the compound with an equatorial leaving group (*cis*-4-*tert*-butylcyclohexyl *p*-bromobenzenesulfonate), the  $\beta$ - $d_4$  isotope effects are substantial, while they are very small or inverse for the corresponding trimethylsilyl compound. The magnitude of these isotope effects approaches that observed in the similar *trans*-4-

*tert*-butylcyclohexyl *p*-bromobenzenesulfonate (equatorial leaving group). In the case of *trans*-3-*tert*-butylcyclohexyl *p*-bromobenzenesulfonate (axial leaving group), the  $\beta$ - $d_4$  isotope effects are even larger than in the *cis* isomer. Their magnitudes are similar to those observed in *trans*-3-(trimethylsilyl)cyclohexyl *p*-bromobenzenesulfonate and in *cis*-4-*tert*-butylcyclohexyl *p*-bromobenzenesulfonate solvolyses. These results confirm that these three substances are reacting by very similar processes. Furthermore, the large magnitude of these isotope effects suggests that  $\beta$ -hydrogen participation or elimination must be involved in the rate-determining step.

The products of the solvolyses of the 3-*tert*-butylcyclohexyl compounds are shown in Table III. Elimination from the carbonium ion appears to be the predominant process in each case, with a small amount of substitution also being observed, and the percentage of elimination is higher with an axial leaving group than with an equatorial leaving group. Stereochemical analyses of the substitution products reveal predominant inversion of configuration, particularly in ethanolic solvents. These results are in accord with those reported previously for the solvolysis of isomeric 4-*tert*-butylcyclohexyl arenesulfonates.<sup>40</sup> As can be seen from ethanol-TFE plots, the solvolysis of alkyl-substituted cyclohexyl brosylates proceeds with substantial assistance by the more nucleophilic solvent.<sup>31,41</sup> Such assistance might involve hydrogen-bonding by solvent at the  $\beta$ -carbon<sup>42</sup> (most of the products involve  $\beta$ -hydrogen elimination or migration) or solvation at the  $\alpha$ -carbon. Substitution in the more nucleophilic ethanol solvents is stereospecific, while that in trifluoroethanol-water mixtures is not. In trifluoroethanolic solvents, nucleophilic or basic attack by solvent should be slower, allowing more complete dissociation of the ion-pair intermediates. This dissociation would allow for a more equal distribution between inverted and retained products.

Oxygen scrambling is very small in the 3-*tert*-butylcyclohexyl brosylates. These results coupled with large  $\beta$ -deuterium isotope effects suggest that ionization to yield an intimate ion pair is the rate-determining step in this process. Hyperconjugation, with or without participation, particularly in the *trans* isomer, is very large, consistent with results observed previously.<sup>13,14</sup>

## Experimental Section

**3-(Trimethylsilyl)cyclohexanone.** The method used was based on methods published by Dunogues et al.<sup>16</sup> and Wickham et al.<sup>17</sup> A 500-mL, three-necked, round-bottom flask containing a magnetic stirring bar, a thermometer, and a condenser was assembled and flushed with dry argon. Tetrahydrofuran (300 mL), which had been previously dried and distilled, was added to the flask. Lithium wire (3.3 g, 0.48 mol) was cut into 0.5-in. segments and weighed in mineral oil. The segments of lithium wire were then rolled, by using a 1-in.-diameter stainless steel rod, into thin ribbons. The ribbons were rinsed in tetrahydrofuran and transferred to the reaction flask. An addition funnel containing chlorotrimethylsilane (52.9 g, 0.487 mol) was attached, and chlorotrimethylsilane was added dropwise to the reaction flask. As the addition continued, effervescence was observed. The temperature of the reaction medium remained below  $30^\circ\text{C}$ . When the addition of chlorotrimethylsilane was complete, an ice-salt bath was placed around the reaction flask, and the reaction mixture was cooled to below  $0^\circ\text{C}$ . 2-Cyclohexenone, which had been purified by vacuum distillation, (21.2 g, 0.221 mol) was added to the addition funnel. The ketone was added dropwise to the

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reaction mixture, while care was taken to maintain the reaction temperature below 5 °C. During the course of this addition, the lithium metal became shiny and then black. When the addition of the ketone was complete, the reaction was allowed to warm slowly to room temperature and allowed to stand, with stirring under an argon atmosphere, overnight.

After standing, nearly all of the lithium metal had disappeared, and a quantity of white precipitate could be observed. The unreacted lithium and the precipitate were removed by vacuum filtration. Excess tetrahydrofuran was removed by using a rotary evaporator. The oily residue was filtered under vacuum to remove additional solid materials. The oily residue was dissolved in 100 mL of tetrahydrofuran and stirred with 100 mL of 10% hydrochloric acid for over an hour. An additional 100 mL of water was added to the mixture, and the solution was extracted with three 50-mL portions of diethyl ether. The ether extract was dried over magnesium sulfate.

After it had been dried, the solution was vacuum filtered through a filter packed with Celite and silica gel. The solution was evaporated on a rotary evaporator. The residue was purified by high-pressure liquid chromatography on a hand-packed glass column packed with silica gel, using a solvent mixture consisting of 70% hexane and 30% ethyl acetate. Solvent was removed from the fraction containing the desired ketone by using a rotary evaporator. Carbon tetrachloride was added to ensure complete removal of residual ethyl acetate as the CCl<sub>4</sub>-ethyl acetate azeotrope, giving the product (16.2 g, 43.0% yield): <sup>1</sup>H NMR (360 MHz, CDCl<sub>3</sub>)  $\delta$  1.05, 1.40, 1.70, 1.78, 2.08, 2.15, 2.25, and 2.30 ppm for ring hydrogens and  $\delta$  -0.029 ppm for the trimethylsilyl hydrogens; <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  -3.79, 25.94, 27.95, 29.88, 41.89, 42.33, and 212.79 ppm.

**cis-3-(Trimethylsilyl)cyclohexanol.** This method was based on that published by Fessenden et al.<sup>6</sup> Lithium aluminum hydride (0.0532 g, 0.00140 mol) was dissolved in 10 mL of anhydrous ether and placed in a dry 50-mL, two-neck flask, which was equipped with a magnetic stirrer. 3-(Trimethylsilyl)cyclohexanone (0.608 g, 0.00360 mol) was dissolved in 5 mL of anhydrous ether and placed in an addition funnel, which was sealed with a drying tube and attached to the reaction flask. The ketone solution was added dropwise to the stirred hydride. After the addition was complete, the reaction was allowed to stir for an additional 30 min.

The excess hydride was destroyed by the careful addition of 0.1 mL of water. The reaction mixture was hydrolyzed by the addition of 0.1 mL of 3 N sodium hydroxide and 0.3 mL of water. The solution was vacuum filtered, and the ether layer was dried over magnesium sulfate.

The ether was removed from the solution with a rotary evaporator, and the product was purified by high-pressure liquid chromatography, using a silica gel column and a 70% hexane-30% ethyl acetate solvent system. The desired fractions were concentrated on a rotary evaporator, using carbon tetrachloride to ensure complete removal of residual ethyl acetate as the carbon tetrachloride-ethyl acetate azeotrope. Products isolated in the chromatography were identified as *trans*-3-(trimethylsilyl)cyclohexanol (0.052 g, 7.5% yield) and *cis*-3-(trimethylsilyl)cyclohexanol (0.293 g, 46.9% yield); overall percentage yield 54.4%. The isomers were characterized by <sup>13</sup>C NMR (75 MHz): *trans*, 66.34 ppm (carbon 1); *cis*, 72.04 ppm (carbon 1).

***trans*-3-(Trimethylsilyl)cyclohexanol.** The method used was based on methods published by Brown et al.<sup>18,43</sup> A 100-mL, two-neck flask, equipped with a pressure-equalizing addition funnel, a gas inlet tube, and a magnetic stirrer was assembled and flushed with a stream of dry argon. A septum cap was attached to the top of the addition funnel. Lithium tri-*sec*-butylborohydride (L-Selectride; 3.0 mL of a 1 M solution in tetrahydrofuran, 0.0030 mol) was introduced into the flask by using a syringe, and the solution was cooled to -78 °C. 3-(Trimethylsilyl)cyclohexanone (0.5039 g, 0.002958 mol) was dissolved in 1.5 mL of distilled, dry tetrahydrofuran and placed in the addition funnel. The ketone solution was added dropwise to the stirred solution, while the flask was maintained at -78 °C. After the addition was complete, the solution was stirred at -78 °C for an additional 3 h, after which it was allowed to warm slowly to room temperature overnight.

The reaction mixture was hydrolyzed by adding 15 mL of 3.0 M sodium hydroxide, followed by 15 mL of 30% hydrogen peroxide. The reaction mixture was saturated with potassium carbonate, and the organic layer was separated and dried over magnesium sulfate. The dried solution was concentrated on a rotary evaporator, and the residue was purified by high-pressure liquid chromatography, using a mixture of 70% hexane and 30% ethyl acetate as the eluent on a silica gel column. The fractions containing the desired products were concentrated with a rotary evaporator, using added carbon tetrachloride to ensure that residual ethyl acetate was removed azeotropically.

Products identified were *trans*-3-(trimethylsilyl)cyclohexanol (0.2471 g, 48.5%) and *cis*-3-(trimethylsilyl)cyclohexanol (0.0299 g, 5.9%); overall percentage yield 54.4%. The isomers were characterized by <sup>13</sup>C NMR (75 MHz): *trans*, 66.34 ppm (carbon 1); *cis*, 72.04 ppm (carbon 1).

**3-(Trimethylsilyl)cyclohexanone-2,2,6,6-d<sub>4</sub>.** 3-(Trimethylsilyl)cyclohexanone (1.96 g, 0.0115 mol) was placed in a 100-mL round-bottom flask, along with 50 mL of deuterium oxide and a small amount of sodium carbonate. A reflux condenser equipped with a drying tube was attached, and the mixture was heated under reflux for about 3 h. The solution was cooled and extracted four times with ether. The ether was removed on a rotary evaporator, and the residue was combined with a fresh 50-mL portion of deuterium oxide, along with a small amount of sodium carbonate. The solution was treated as above for a total of four exchange processes.

The final product was isolated, yielding 1.35 g (0.00776 moles) of deuterated ketone, 67.6% yield: <sup>1</sup>H NMR (360 MHz, CDCl<sub>3</sub>)  $\delta$  -0.03 ppm [9, trimethylsilyl protons], 1.04 [1], 1.41 [1], 1.69 [1], 1.79 [1], and 2.16 ppm [1, ring protons]. No peaks arising from residual protons in the 2- and 6-positions could be observed. The mass spectrum showed a strong molecular ion peak at *m/e* = 174. The complex nature of fragmentation patterns precludes a precise isotopic analysis by mass spectrometry, however. On the basis of spectral evidence, one may conclude that the product is more than 95% deuterated.

***cis*-3-(Trimethylsilyl)cyclohexanol-2,2,6,6-d<sub>4</sub>.** This compound was prepared by the same method reported above for *cis*-3-(trimethylsilyl)cyclohexanol, using 3-(trimethylsilyl)cyclohexanone-2,2,6,6-d<sub>4</sub> as the starting material; yield of product 0.288 g, 46.9%. The product was characterized by <sup>13</sup>C NMR (75 MHz): 72.04 ppm (carbon 1).

***trans*-3-(Trimethylsilyl)cyclohexanol-2,2,6,6-d<sub>4</sub>.** This compound was prepared by the same method reported above for *trans*-3-(trimethylsilyl)cyclohexanol, using 3-(trimethylsilyl)cyclohexanone-2,2,6,6-d<sub>4</sub> as the starting material; yield of product 0.312 g, 52.0%. The product was characterized by <sup>13</sup>C NMR (75 MHz): 66.34 ppm (carbon 1).

***cis*-3-(Trimethylsilyl)cyclohexanol-1-d.** This compound was prepared by a method similar to that reported above for *cis*-3-(trimethylsilyl)cyclohexanol, using 3-(trimethylsilyl)cyclohexanone and lithium aluminum deuteride as the starting materials; yield of product 0.766 g, 38.2%. The product was characterized by <sup>13</sup>C NMR (75 MHz): 72.04 ppm (carbon 1).

***trans*-3-(Trimethylsilyl)cyclohexanol-1-d.** This product was prepared according to a method based on that published by Zweifel and Brown.<sup>19</sup> 3-(Trimethylsilyl)cyclohexanone (3.00 g, 0.0176 mol) was dissolved in 2 mL of purified Diglyme and placed in a flame-dried, 50-mL, two-neck flask. A stream of dry argon was passed through the flask. Boron trifluoride etherate (1.2 mL, 1.4 g, 0.0098 mol) was also added to the flask. A solution of sodium borodeuteride (0.306 g, 0.00732 mol) in 7.5 mL of purified Diglyme was added dropwise to the stirring reaction mixture. After the addition was complete, the reaction mixture was allowed to stand under an argon atmosphere overnight.

The excess hydride was decomposed by the addition of 0.6 mL of water. The reaction mixture was hydrolyzed by the addition of 0.7 mL of 3 N sodium hydroxide, followed by 0.7 mL of 30% hydrogen peroxide. The solution was allowed to stand, with stirring, for over an hour. The reaction mixture was taken up in 5 mL of ether and extracted five times with water. The ether solution was dried over magnesium sulfate.

The drying agent was removed by vacuum filtration through Celite, and the solution was concentrated on a rotary evaporator. The residue was separated by high-pressure liquid chromatog-

raphy using a silica gel column and a 70% hexane–30% ethyl acetate solvent mixture. Two isomeric alcohols were obtained: *trans*-3-(trimethylsilyl)cyclohexanol-1-*d* (0.362 g, 11.9%) and *cis*-3-(trimethylsilyl)cyclohexanol-1-*d* (0.570 g, 18.7%); overall percentage yield 30.6%. The isomers were characterized by  $^{13}\text{C}$  NMR (75 MHz): *trans*, 66.34 ppm (carbon 1); *cis*, 72.04 ppm (carbon 1).

***cis*- and *trans*-3-*tert*-Butylcyclohexanol.** These products were prepared by a method based on that published by Meyers et al.<sup>28</sup> 3-*tert*-Butylphenol (Aldrich, 7.98 g, 0.0531 mol) was placed in a 500-mL glass bottle, along with 4.0 g of 5% rhodium on powdered alumina catalyst and 100 mL of reagent-grade absolute methanol. All metal parts of a Parr low-pressure hydrogenation shaker apparatus were cleaned with acetone, and all rubber parts were soaked overnight in 35% sodium hydroxide solution. Hydrogen gas was admitted to the sealed bottle at 57 psi of pressure, and the reaction was allowed to proceed for 12 h. Within 2 h, the pressure in the vessel dropped to 35 psi, and the pressure remained relatively constant thereafter.

After the reaction, the apparatus was disassembled, and the catalyst was removed from the reaction mixture by two successive gravity filtrations. Methanol was removed by using a rotary evaporator. The residue was shown by NMR spectroscopy to be the desired mixture of *cis*- and *trans*-3-*tert*-butylcyclohexanol (7.89 g, 95.0%). Separation by high-pressure liquid chromatography was achieved using a silica gel column with a 70% hexane–30% ethyl acetate solvent mixture, and the *trans* to *cis* ratio for the hydrogenation was shown to be 67.6% to 32.4%. *trans*-3-*tert*-Butylcyclohexanol: mp 67.5–68.0 °C;  $^1\text{H}$  NMR (360 MHz,  $\text{CDCl}_3$ )  $\delta$  4.19 ppm (quintet, hydrogen on carbon 1);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ) 67.33 ppm (carbon 1). *cis*-3-*tert*-Butylcyclohexanol: mp 40.5–41.5 °C;  $^1\text{H}$  NMR (360 MHz,  $\text{CDCl}_3$ )  $\delta$  3.57 ppm (multiplet, hydrogen on carbon 1);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ) 71.70 ppm (carbon 1).

**3-*tert*-Butylcyclohexanone.** The product was prepared by the method of Djerassi et al.<sup>29</sup> A mixture of *cis*- and *trans*-3-*tert*-butylcyclohexanol (8.0 g, 0.051 mol) was placed in a 250-mL round-bottom flask fitted with a magnetic stirring bar and a condenser. Acetone (15 mL) was added to the flask. A solution containing 4.5 g of chromium trioxide in 15 mL of water and 3.75 mL of concentrated sulfuric acid was prepared and placed in an addition funnel. The reaction vessel was cooled with an ice–water bath. The chromium trioxide–acid solution was added dropwise to the reaction over a period of an hour, and small amounts of magnesium sulfate were also added to the reaction mixture every 20–30 min during the acid addition. The reaction mixture changed color from green to orange during the addition. After the addition of acid was complete, the reaction was allowed to stir for an additional hour, with the temperature being maintained between 5 and 10 °C.

The reaction mixture was neutralized with solid sodium bicarbonate, and the solution was filtered by gravity and dried over magnesium sulfate. The acetone solvent was removed with a rotary evaporator. Yield of product 4.2 g, 53.2%;  $^1\text{H}$  NMR (90 MHz,  $\text{CDCl}_3$ )  $\delta$  2.19 (multiplet), 0.97–0.66 (multiplets), 0.89 ppm (singlet);  $^{13}\text{C}$  NMR (22.50 MHz,  $\text{CDCl}_3$ ) 212.26, 49.41, 43.61, 41.23, 32.67, 27.20, 26.22, and 25.63 ppm.

***trans*-3-*tert*-Butylcyclohexanol.** This compound was prepared by a method based on that used for the preparation of *trans*-3-(trimethylsilyl)cyclohexanol. 3-*tert*-Butylcyclohexanone (0.3559 g, 0.002307 mol) was reduced with 2.3 mL of a 1 M solution of lithium tri-*sec*-butylborohydride (L-Selectride) in tetrahydrofuran. After purification by high-pressure liquid chromatography, using a mixture of 70% hexane and 30% ethyl acetate as the eluent on a silica gel column, 0.2183 g (60.7% yield) of the desired product was obtained.

**3-*tert*-Butylcyclohexanone-2,2,6,6-*d*<sub>4</sub>.** 3-*tert*-Butylcyclohexanone (1.99 g, 0.013 mol) was placed in a 100-mL round-bottom flask, along with 15 mL of deuterium oxide and a small amount of sodium carbonate. A reflux condenser equipped with a drying tube was attached, and the mixture was heated under reflux overnight. The solution was cooled and extracted four times with ether. The ether was removed on a rotary evaporator, and the residue was combined with a fresh 15-mL portion of deuterium oxide, along with a small amount of sodium carbonate. The solution was treated as above for a total of four exchange processes.

The final product was isolated, yielding 0.745 g (0.0047 mol) of deuterated ketone, 36.5% yield. The  $^1\text{H}$  NMR (360 MHz,  $\text{CDCl}_3$ ) spectrum shows a strong simplification of the pattern from 1.9 to 2.5 ppm, including a nearly complete absence of peaks at 2.32 and 2.42 ppm, indicating essentially complete deuteration. The  $^{13}\text{C}$  NMR spectrum (75 MHz,  $\text{CDCl}_3$ ) shows the multiplicity characteristic of deuteration at 41 and 43 ppm. The extent of deuteration is, therefore, assumed to be in excess of 95%.

***cis*-3-*tert*-Butylcyclohexanol-2,2,6,6-*d*<sub>4</sub>.** This compound was prepared by a method based on that used for the synthesis of *cis*-3-(trimethylsilyl)cyclohexanol. 3-*tert*-Butylcyclohexanone-2,2,6,6-*d*<sub>4</sub> (0.3974 g, 0.00251 mol) was reduced with lithium aluminum hydride (0.0322 g, 0.001578 mol). Purification of the product by high-pressure liquid chromatography, using a mixture of 70% hexane and 30% ethyl acetate as the eluent on a silica gel column, yielded the product (0.37 g, 92.0% yield).

***trans*-3-*tert*-Butylcyclohexanol-2,2,6,6-*d*<sub>4</sub>.** This compound was prepared by a method based on that used for the preparation of *trans*-3-(trimethylsilyl)cyclohexanol. 3-*tert*-Butylcyclohexanone-2,2,6,6-*d*<sub>4</sub> (0.348 g, 0.00220 mol) was reduced with 2.2 mL of a 1 M solution of lithium tri-*sec*-butylborohydride (L-Selectride) in tetrahydrofuran. After purification by high-pressure liquid chromatography, using a mixture of 70% hexane and 30% ethyl acetate as the eluent on a silica gel column, 0.21 g (59.6% yield) of the desired product was obtained.

***cis*- and *trans*-3-*tert*-Butylcyclohexanol-1-*d*.** The mixture of isomers was prepared by a method similar to that used for the preparation of *cis*-3-(trimethylsilyl)cyclohexanol-1-*d*. 3-*tert*-Butylcyclohexanone (2.5 g, 0.016 mol) was reduced with 0.25 g (0.0057 mol) of lithium aluminum deuteride. The isomers were separated by high-pressure liquid chromatography, using a mixture of 70% hexane and 30% ethyl acetate as the eluent on a silica gel column. The product yields were *cis* isomer 2.26 g, 87.5% yield, and *trans* isomer 0.31 g, 12.5% yield. Careful analysis by  $^1\text{H}$  NMR (360 MHz) showed the *cis* isomer to be approximately 58% deuterated in the  $\alpha$ -positions. The extent of deuteration was judged to be sufficient for product study experiments but not sufficient for kinetic studies or isotope effect determination.

***p*-Bromobenzenesulfonates.** *p*-Bromobenzenesulfonates of each of the above alcohols were prepared by a method based on that of Tipson.<sup>20</sup>

***p*-Bromobenzene- $^{18}\text{O}$ -sulfonates.** *para*-Bromobenzene- $^{18}\text{O}$ -sulfonates of *cis*- and *trans*-3-(trimethylsilyl)cyclohexanol and *cis*- and *trans*-3-*tert*-butylcyclohexanol were prepared by a method based on that of Tipson,<sup>20</sup> using *p*-bromobenzenesulfonyl chloride- $^{18}\text{O}$  as a reagent.<sup>44</sup>

**Conductivity Water.** Deionized water was prepared by the procedure described by Murr.<sup>45</sup>

**Ethanol (E).** Ethanol (E) was prepared by the procedure described by Murr,<sup>45</sup> with modifications by Buddenbaum.<sup>46</sup>

**2,2,2-Trifluoroethanol.** 2,2,2-Trifluoroethanol (TFE or T) was prepared by the procedure described by Shiner et al.<sup>47</sup>

**Ethanol–Water.** These volume percent solutions were prepared by weight with densities and buoyancy corrections as described by Murr.<sup>45</sup>

**2,2,2-Trifluoroethanol–Water.** These solutions were prepared as weight percent solutions by the method described by Shiner et al.<sup>47</sup>

**Conductance Kinetics Procedure.** Conductance measurements were taken using a bipolar pulsed conductance apparatus built in this laboratory, based on the design of Casserta et al.<sup>22</sup> The calibration was performed by the method described by Wilgis.<sup>44</sup> Conductivity cells used were made in the laboratory on the basis of the design of Murr,<sup>45</sup> using modifications by Dowd,<sup>48</sup> Tomasik,<sup>49</sup> and Wilgis.<sup>44</sup> The data were recorded by a TI 980 computer using programs developed by McMullen<sup>50</sup> and Tomasik<sup>49</sup> or by an IBM-PC computer using programs developed

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by Ensinger.<sup>51</sup> The data were analyzed on an IBM-PC computer, using a calibration program written by Tomasik<sup>49</sup> and Wilgis<sup>44</sup> and a nonlinear, doubly weighted least-squares program written by Buddenbaum,<sup>46</sup> with modifications by Vogel,<sup>52</sup> Pinnick,<sup>53</sup> Bowersox and Tomasik,<sup>54</sup> and Wilgis.<sup>44</sup>

**Product Determination.** Product studies by <sup>2</sup>H NMR spectroscopy were performed in the following manner. A 1.0-mL sample of reaction mixture (approximately 0.1 M in deuterium) with a molar excess of 2,6-lutidine was prepared in a 1.0-mL volumetric flask. The solution was transferred to an NMR tube, sealed, and allowed to react for at least 10 half-lives. The <sup>2</sup>H NMR spectra were recorded by using a Nicolet 360-MHz spectrometer at 55.4 MHz. The Fourier transform NMR spectra were taken by using between 500 and 1000 scans. Product ratios were determined by comparison of the weighed cutouts of the peaks.

Chemical shifts for products, which varied slightly with solvent, were as follows in 97T: bicyclo[3.1.0]hexane (*1-d*,  $\delta$  1.44; 2,2,6,6-*d*<sub>4</sub>,  $\delta$  0.42, 1.95); cyclohexene (*1-d*,  $\delta$  6.0; 3-*d*,  $\delta$  2.22; 4,4-*d*<sub>2</sub>,  $\delta$  1.70); 3-(trimethylsilyl)cyclohexene (2-*d*,  $\delta$  6.0; 6,6-*d*<sub>2</sub>,  $\delta$  2.2); 4-(trimethylsilyl)cyclohexene (*1-d*,  $\delta$  6.0; 3,3-*d*<sub>2</sub>,  $\delta$  2.2); *cis*-3-(trimethylsilyl)cyclohexanol (*1-d*,  $\delta$  3.78; 2,2,6,6-*d*<sub>4</sub>,  $\delta$  1.34, 1.44, 2.32, 2.33); *trans*-3-(trimethylsilyl)cyclohexanol (*1-d*,  $\delta$  4.32; 2,2,6,6-*d*<sub>4</sub>,  $\delta$  2.0, 1.6, 1.7); *cis*-3-(trimethylsilyl)cyclohexyl trifluoroethyl ether (*1-d*,  $\delta$  3.67; 2,2,6,6-*d*<sub>4</sub>,  $\delta$  1.34, 1.44, 2.32, 2.33); *trans*-3-(trimethylsilyl)cyclohexyl trifluoroethyl ether (*1-d*,  $\delta$  4.2; 2,2,6,6-*d*<sub>4</sub>,  $\delta$  2.0, 1.6, 1.7); 3-*tert*-butylcyclohexene-1-*d* and 4-*tert*-butylcyclohexene-2-*d* ( $\delta$  5.97); *cis*- and *trans*-3-*tert*-butylcyclohexanol and *cis*- and *trans*-3-*tert*-butylcyclohexyl trifluoroethyl ether (*1-d*,  $\delta$  4.10; 2,2,6,6-*d*<sub>4</sub>,  $\delta$  2.10); 3-*tert*-butylcyclohexene-2,2,6,6-*d*<sub>3</sub> and 4-*tert*-butylcyclohexene-1,3,3-*d*<sub>3</sub> ( $\delta$  5.9 and 2.2).

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Coope for <sup>1</sup>H and <sup>2</sup>H NMR spectra, Ford P. Wilgis for <sup>13</sup>C NMR spectra and <sup>18</sup>O analyses, Dr. Lester Taylor for the GC/MS analysis, and Teresa Wright-Kester for <sup>13</sup>C NMR spectra.

**Registry No.** 1, 99810-99-8; 1- $\alpha$ -*d*, 122722-74-1; 1- $\beta$ -*d*<sub>4</sub>, 122722-76-3; 2, 99811-00-4; 2- $\alpha$ -*d*, 122722-75-2; 2- $\beta$ -*d*<sub>4</sub>, 122722-77-4; 3, 122722-65-0; 3- $\beta$ -*d*<sub>4</sub>, 122722-78-5; 4, 122722-66-1; 4- $\beta$ -*d*<sub>4</sub>, 122722-79-6; 5, 966-02-9; 5- $\alpha$ -*d*, 1688-18-2; 5- $\beta$ -*d*<sub>4</sub>, 1099-68-9; 6, 966-01-8; 6- $\alpha$ -*d*, 968-89-8; 6- $\beta$ -*d*<sub>4</sub>, 1099-67-8; 3-(trimethylsilyl)cyclohexanone, 7531-60-4; *cis*-3-(trimethylsilyl)cyclohexanol, 7452-98-4; *trans*-3-(trimethylsilyl)cyclohexanol, 7452-99-5; 3-(trimethylsilyl)cyclohexanone-2,2,6,6-*d*<sub>4</sub>, 122722-67-2; *cis*-3-(trimethylsilyl)cyclohexanol-2,2,6,6-*d*<sub>4</sub>, 109702-24-1; *trans*-3-(trimethylsilyl)cyclohexanol-2,2,6,6-*d*<sub>4</sub>, 109702-25-2; *cis*-3-(trimethylsilyl)cyclohexanol-1-*d*, 122722-68-3; *trans*-3-(trimethylsilyl)cyclohexanol-1-*d*, 122722-69-4; *cis*-3-*tert*-butylcyclohexanol, 10488-10-5; *trans*-3-*tert*-butylcyclohexanol, 16201-66-4; 3-*tert*-butylcyclohexanone, 936-99-2; *cis*-3-*tert*-butylcyclohexanol-2,2,6,6-*d*<sub>4</sub>, 122722-70-7; *trans*-3-*tert*-butylcyclohexanol-2,2,6,6-*d*<sub>4</sub>, 122722-71-8; *cis*-3-*tert*-butylcyclohexanol-1-*d*, 122722-72-9; *trans*-3-*tert*-butylcyclohexanol-1-*d*, 122722-73-0; bicyclo[3.1.0]hexane-1-*d*, 122722-80-9; bicyclo[3.1.0]hexane-2,2,6,6-*d*<sub>4</sub>, 122722-81-0; cyclohexene-1-*d*, 42843-17-4; cyclohexene-3-*d*, 84108-31-6; cyclohexene-4,4-*d*<sub>2</sub>, 122722-82-1; 3-(trimethylsilyl)cyclohexene-2-*d*, 122722-83-2; 3-(trimethylsilyl)cyclohexene-6,6-*d*<sub>2</sub>, 122722-84-3; 4-(trimethylsilyl)cyclohexene-1-*d*, 122722-85-4; 4-(trimethylsilyl)cyclohexene-3,3-*d*<sub>2</sub>, 122722-86-5; *cis*-3-(trimethylsilyl)cyclohexyl trifluoroethyl ether-1-*d*, 122722-87-6; *cis*-3-(trimethylsilyl)cyclohexyl trifluoroethyl ether-2,2,6,6-*d*<sub>4</sub>, 122722-88-7; *trans*-3-(trimethylsilyl)cyclohexyl trifluoroethyl ether-1-*d*, 122722-89-8; *trans*-3-(trimethylsilyl)cyclohexyl trifluoroethyl ether-2,2,6,6-*d*<sub>4</sub>, 122722-90-1; 3-*tert*-butylcyclohexene-1-*d*, 102853-34-9; 4-*tert*-butylcyclohexene-2-*d*, 122722-91-2; *cis*-3-*tert*-butylcyclohexyl trifluoroethyl ether-1-*d*, 122722-92-3; *cis*-3-*tert*-butylcyclohexyl trifluoroethyl ether-2,2,6,6-*d*<sub>4</sub>, 122722-93-4; *trans*-3-*tert*-butylcyclohexyl trifluoroethyl ether-1-*d*, 122722-94-5; *trans*-3-*tert*-butylcyclohexyl trifluoroethyl ether-2,2,6,6-*d*<sub>4</sub>, 122722-95-6; 3-*tert*-butylcyclohexene-2,6,6-*d*<sub>3</sub>, 122722-96-7; 4-*tert*-butylcyclohexene-1,3,3-*d*<sub>3</sub>, 122722-97-8; bicyclohexane, 285-58-5; cyclohexene, 110-83-8; 3-(trimethylsilyl)cyclohexene, 40934-71-2; 4-(trimethylsilyl)cyclohexene, 40934-72-3; 3-*tert*-butylcyclohexene, 14072-87-8; 4-*tert*-butylcyclohexene, 2228-98-0; 3-*tert*-butylcyclohexanone-2,2,6,6-*d*<sub>4</sub>, 122722-98-9.

## An ab Initio Study of Vinylallene Conformations

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Ab initio optimizations and MP2/6-31G\* single-point calculations are performed for the polyene compounds (*Z*)-1,3-pentadiene (5), 1,2,4-pentatriene (6), and (*Z*)-1,2,4-hexatriene (7). The *s*-*trans* conformer is found to predominate in all cases; however, the preference is less for the vinylallenes than for either butadiene or pentadiene. Compound 6 was found to be planar in both the *s*-*trans* and *s*-*cis* conformations; however, nonplanar twist structures for 5 and 7 were found at lower energy than the planar *s*-*cis*. As further evidence of steric crowding in the *s*-*cis* conformation, the methyl group of compounds 5 and 7 are found to stagger rather than eclipse the double bond in the *s*-*cis* conformation. The reduced methyl rotation barrier in the *s*-*trans* pentadiene and hexatriene is found to be a result of steric repulsions and reduced  $\pi$  interactions between the out of plane methyl hydrogens and the  $\pi$  bond. Geometries, orbital energies, and intramolecular interactions are examined with a view to understanding the enhanced reactivities of the vinylallenes. In these, few differences between the normal dienes and the vinylallenes are found.

### Introduction

Vinylallenes have been shown to undergo [1,5]-sigmatropic rearrangements at temperatures lower than those commonly employed for conjugated dienes. For example,

(*Z*)-2-methyl-1,3-pentadiene (1) reacts at 225 °C ( $E_{\text{act}} = 32.8$  kcal/mol),<sup>2</sup> while the corresponding shift occurs at 100 °C in the vinylallene 5-methyl-1,2,4-hexatriene (3) ( $E_{\text{act}} = 24.6$  kcal/mol).<sup>3</sup>

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