# Silane Reductions in Acidic Media. VI. The Mechanism of Organosilane Reductions of Carbonyl Compounds. Transition State Geometries of Hydride Transfer Reactions<sup>1a,b</sup>

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The hydride transfer step in reductions of carbonyl compounds by hindered organosilanes yields alkyl silyl ethers in a four-center process involving the silicon hydride and the protonated carbonyl group. Rapid equilibration between silyl ether, alcohol, and silyl trifluoroacetate occurs in trifluoroacetic acid when triethylsilane is employed. Subsequent reactions of alcohol, silyl ether, and silyl trifluoroacetate products are identified. The implications of these results for the stereoselectivities of hydride transfer to substituted cyclohexanones are discussed. The sensitivity of bulky reducing agents toward 2-methyl and axial 3,5 substituents is proposed to result from differences in the transition state geometries for the hydride transfer step. The mechanism for the formation of alkyl ethers in silane reductions is also discussed.

Organosilanes are effective reducing agents for the carbonyl group of aldehydes and ketones when these reactions are performed in acidic media. The nature of the hydride transfer step has not, however, been investigated. Such information would have particular relevance to an understanding of the stereoselectivity in ketone reductions by organosilanes<sup>2</sup> and to potential uses of organosilanes in selective syntheses.

Two mechanisms can be considered for the hydride transfer step in carbonyl group reductions by organosilanes performed in Bronsted acids, the media usually employed for these reactions. In Scheme I (counterion mechanism)

$$R_2C = O + HA \implies R_2C = OH^* + A^-$$
(1)

$$R_2C = OH^+ + A^- + R'_{3}SiH \longrightarrow R_2CHOH + R'_{3}SiA \quad (2)$$

nucleophilic substitution by the counterion  $(A^-)$  of the acid used to catalyze the reaction is involved in the rate-limiting hydride transfer step (eq 2). When the anion of the Bronsted acid is relatively nonnucleophilic, an additional step, involving alcohol in the displacement of hydrogen from silicon through a chain process (eq 3), may be important. Either inversion or retention of configuration at silicon may be involved by analogy to the stereochemical course of hydride transfer in comparable organosilane reactions.<sup>4-9</sup>

$$R_2C = OH^+ + R_2CH - OH + R'_3SiH \rightarrow R_2CHOH + R'_3SiOCHR_2 + H^+ \quad (3)$$

In the alternate mechanism for alcohol formation (Scheme II, four-center mechanism) nucleophilic attack by

$$R_2 C = O + HA \longrightarrow R_2 C = OH^* + A^*$$
(1)

$$R_2C = OH^{\star} + R'_3SiH \longrightarrow R_2CHOSiR'_3 + H^{\star}$$
 (4)

$$R_2CHOSiR'_3 + HA \longrightarrow R_2CHOH + R'_3SiA$$
 (5)

the oxygen of the carbonyl group occurs with hydride transfer to the carbonyl carbon. Subsequent solvolysis of the silyl alkyl ether forms the alcohol product. A similar mechanism for hydride transfer has been suggested for the deoxygenation of sulfoxides by silanes,<sup>10</sup> and to explain the retention of configuration at silicon observed in reductions of silyl derivatives by isobutylaluminum hydride.<sup>11</sup>

The fundamental difference between the mechanisms for silane reductions of carbonyl compounds in Schemes I and II is the nucleophile that displaces hydride from silicon. In Scheme II the nucleophile is the oxygen of the carbonyl group; the first-formed reaction product is an alkyl silyl ether. In Scheme I the anion of the protonic acid is the nucleophile; alcohol and  $R_3SiA$  are formed in the hydride transfer step. Alternatively, from eq 3, silyl ether should be the dominant reaction product; in this case, however, if a structurally different alcohol is employed in the ketone reduction, the nucleophilic alcohol need not be identical with that produced by hydride transfer. Thus the reaction products produced directly in the hydride transfer step differentiate between the pathways for silane reduction.

In this paper we wish to report the results of our studies on the mechanism of the hydride transfer step in silane reductions of carbonyl compounds and on the subsequent fate of reaction intermediates in trifluoroacetic acid media. The implications of these results for the stereoselectivities of hydride transfer to substituted cyclohexanones are discussed.

#### Results

The determination of the rate-limiting step in organosilane reductions is a complex problem owing to the nature of the reaction medium. The first-formed reduction products may subsequently react to form additional products suggestive of alternative mechanistic pathways. To minimize such difficulties trifluoroacetic acid was chosen as the Bronsted acid, and minimal amounts of this acid were employed in order to decrease the rates of reactions subsequent to the rate-limiting step.

An additional complication was suggested in studies at room temperature of the reduction of 4-*tert*-butylcyclohexanone by triethylsilane in which only 1 equiv of trifluoroacetic acid was employed. The data obtained from these studies<sup>12</sup> suggested that a exchange process of silyl alkyl ether and trifluoroacetic acid with alcohol and silyl trifluoroacetate (eq 6, R = 4-*tert*-butylcyclohexyl) was occurring.<sup>13</sup> The unsubstituted cyclohexyl system was chosen to examine this process in greater detail.

$$ROSiEt_3 + CF_3CO_2H \stackrel{K}{\rightleftharpoons} ROH + Et_3SiO_2CCF_3 \quad (6)$$

Either treatment of cyclohexyl triethylsilyl ether with trifluoroacetic acid or mixing cyclohexanol and triethylsilyl trifluoroacetate in trifluoroacetic acid resulted in the same equilibrium mixture of products (eq 6, R = cyclohexyl, K = $1.4 \pm 0.2$ ). When 10 equiv of trifluoroacetic acid based on either silyl ether or silyl trifluoroacetate was used, equilibrium was achieved within 25 sec; when 1 equiv of trifluoroacetic acid was used, equilibration occurred only after a reaction period of 5 min. Yields of solution components

 
 Table I

 Di-tert-butylmethylsilane Reduction of 4-tert-Butylcyclohexanone<sup>a</sup>

Time, min	% reduction <sup>b</sup>	Yield, %				
		ROSiMe- (t-Bu)	ROH	Alkened	RO <sub>2</sub> CCF <sub>3</sub>	
35	62	54	8	<1	<1	
60	88	68	5	4	11	
160	91	68	. 3	5	15	
344	94	63	2	7	22	
22 hr	100	58	ō	8	34	

<sup>*a*</sup> Reduction was run at room temperature with 1.0 mmol of 4-*tert*-butylcyclohexanone (98-53-3), 0.75 mmol of di*tert*-butylmethylsilane (56310-20-4), and 1.5 mmol of trifluoroacetic acid. <sup>*b*</sup> Based on reacted silane. <sup>*c*</sup> Actual product yields based on <sup>1</sup>H NMR analyses and confirmed by GLC methods. Isomeric yields were comparable to those previously observed.<sup>1a</sup> R = 4-*tert*-butylcyclohexyl. <sup>*d*</sup> 4-*tert*-Butylcyclohexene.

were determined at more than four different times for each of four separate reactions. The formation of cyclohexyl trifluoroacetate from cyclohexanol occurred at a slower rate than the interconversion between silyl ether and alcohol. Triethylsilyl trifluoroacetate was converted to hexaethyldisiloxane by the water produced from the trifluoroacetolysis of cyclohexanol.

The value of K obtained for the cyclohexyl system is nearly identical with that calculated for the 4-*tert*-butylcyclohexyl system ( $K = 1.7 \pm 0.2$ ). In either system the alcohol product is favored over the silyl ether, and the equilibrium exchange described in eq 6 is rapidly attained even when minimal amounts of trifluoroacetic acid are used.

The rapid equilibration of triethylsilyl ether and alcohol in trifluoroacetic acid sets a severe limitation on the determination of the mechanism for hydride transfer in triethylsilane reductions. At equilibrium it is not possible to determine from which direction equilibration has been achieved. However, prior to equilibrium observation of a value for the ratio, [ROH][Et<sub>3</sub>SiO<sub>2</sub>CCF<sub>3</sub>]/[ROSi- $Et_3$ [CF<sub>3</sub>CO<sub>2</sub>H], that is greater than the equilibrium value would be suggestive of the counterion mechanism (Scheme I), whereas if the ratio is less than the equilibrium value, the four-center mechanism (Scheme II) or hydride transfer by eq 3 would be implied. Attempts to determine the direction from which equilibration occurs in the reduction of cvclohexanone by triethylsilane were unsuccessful. Equilibrium (eq 6, R = cyclohexyl) was established prior to 5 min reaction times (<2% reduction) even when only 0.5 equiv of trifluoroacetic acid was employed.

When the rate of equilibration of silyl ether-alcohol is comparable to the rate of reduction, as in the case of cyclohexanone reductions by triethylsilane, the mechanism of the hydride transfer step cannot be determined with confidence. However, a reliable distinction between Schemes I and II is attainable if (1) the rate of reduction is faster than the rate of equilibration and (2) the reduction product is not the predominant form at equilibrium. From previous studies both criteria appeared possible in reactions with *tert*-butylsilanes.<sup>1a</sup> Both di-*tert*-butylmethylsilane and tri*tert*-butylsilane yield silyl ethers as the exclusive or nearly exclusive reduction product at short reaction times (<50% reduction) in reactions with cyclohexanones.

The reduction of 4-*tert*-butylcyclohexanone by di-*tert*butylmethylsilane was performed and the reaction products analyzed at various times to determine the exact levels of silyl ether and alcohol present during reduction.<sup>14</sup> The results of this study are given in Table I and clearly show that silyl ether and alcohol are the initially formed reaction products. However, although the relative yield of the silyl ether is as high as 87%, indicating that this compound is the primary reduction product, the ratio of alcohol to silyl ether may in fact reflect the relative equilibrium concentrations of these two components under the reaction conditions employed.

To determine the extent of the silvl ether-alcohol interconversion (eq 7) di-tert-butylmethylsilyl trifluoroacetate was prepared and added to an equal amount of 4-tertbutylcyclohexanol (26% cis, 74% trans), followed by 3 equiv of trifluoroacetic acid. After 20 and 280 min, a longer time than was required for complete reduction of 4-tert-butylcyclohexanone,<sup>1a</sup> no 4-tert-butylcyclohexyl di-tert-butylmethylsilyl ether was observed. Only 4-tert-butylcyclohexanol, the corresponding trifluoroacetates, and the silvl trifluoroacetate were detected, indicating that, if equilibration occurred, the equilibrium constant for eq 7 must be greater than 50. In reductions of 4-tert-butylcyclohexanone by di-tert-butylmethylsilane under comparable conditions the product ratio from eq 7 was observed to be less than 0.005, a factor of 10000 from the minimum estimate of the equilibrium value. From these experiments, which show that the silvl ether is the first-formed reduction product, a distinction between Schemes I and II can be made. However, these data do not permit a choice between eq 3 and 4 for the hydride transfer step.

$$R_2 CHOSiMe(t-Bu)_2 + CF_3 CO_2 H \rightleftharpoons$$

$$R_2 CHOH + (t-Bu)_2 MeSiO_2 CCF_3 \quad (7)$$

In a separate experiment 4-tert-butylcyclohexanone was reduced by di-tert-butylmethylsilane in the presence of 0.84 equiv of trans-4-methylcyclohexanol. Analysis of the reaction products throughout the time for complete reduction showed the presence of cis- and trans-4-tert-butylcyclohexyl di-tert-butylmethylsilyl ether (74% cis at 16% reduction) and other reaction components previously observed in the reduction of 4-tert-butylcyclohexanone. No trace of trans-4-methylcyclohexyl di-tert-butylmethylsilyl ether, the silyl ether product expected from eq 3, could be detected. Under the same reaction conditions 4-methylcyclohexanone yielded the isomeric 4-methylcyclohexyl ditert-butylmethylsilyl ethers at levels comparable to those for the 4-tert-butylcyclohexyl silyl ethers observed in reductions of 4-tert-butylcyclohexanone.

Separate experiments were performed to determine if the symmetrical ethers formed by silane reductions in trifluoroacetic acid could be produced in reactions involving silyl alkyl ethers or alcohols. A mechanism for symmetrical ether formation has been previously described and requires hydride transfer to an O-alkylated carbonyl compound.<sup>15</sup> Symmetrical ethers were not produced within the limits of detectability from the reaction of alcohol with trifluoroacetic acid, from a mixture of alcohol and trifluoroacetic acid, from silyl alkyl ethers in trifluoroacetic acid, or from mixtures of silyl alkyl ethers and alcohols in trifluoroacetic acid. Symmetrical ethers are formed by reduction rather than by substitution on silyl alkyl ethers or alcohols.

### Discussion

The mechanism for alcohol formation in reductions of carbonyl compounds by di- and tri-*tert*-butylsilanes is adequately described by Scheme II. The hydride-transfer step occurs in a four-center arrangement between the protonated carbonyl group and the silicon hydride and does not involve either the counterion of the acid employed or the alcohol formed during the reduction process. Owing to the rapid equilibration between alcohol and silyl ether (eq 6), however, the mechanism of the hydride transfer step with less hindered silanes, such as triethylsilane, could not be directly determined with confidence by the same method successfully used with more hindered silanes.

The hydride transfer step resulting in symmetrical ethers is consistent with that of the counterion mechanism (eq 8,  $A^-$  = alcohol or conjugate base of acid). Neither silyl ethers nor alcohols are directly converted to ethers under the same reaction conditions used for reductions of carbonyl compounds. The relative yield of symmetrical ether is dependent not only on the concentration of alcohol, but also, on the relative rates for hydride transfer to protonated and O-alkylated carbonyl compound.

$$R_2C = OR' + R''_3SiH + A^- \rightarrow R_2CHOR' + R''_3SiA \quad (8)$$

A general mechanism for silane reductions of carbonyl compounds in Bronsted acids is given in Scheme III. Acti-

Scheme III  

$$R_2C = O + HA \implies R_2C = OH + A^-$$
  
 $R_2C = OH + R'_3SiH$   
 $A^-$   
 $R_2CHOH + R'_3SiH$   
 $R_2CHOH + HA \implies R_2CHA + H_2O$   
 $R'_3SiA + H_2O \implies R'_3SiOH + HA$   
 $R'_3SiA + R'_3SiOH \longrightarrow (R'_3Si)_2O + HA$ 

vation of the carbonyl group is usually required before hydride transfer can occur.<sup>16</sup> When protonic acids are used to catalyze silane reductions, these acids are also involved in subsequent reactions of the primary reduction products. These secondary reactions occur by displacement at silicon; displacement at carbon is not involved.<sup>17</sup> Lewis acids, such as zinc chloride<sup>18</sup> and aluminum chloride,<sup>19</sup> also catalyze silane reduction yielding mainly alkyl silyl ethers, presumably by a four-center mechanism; however, these reactions are similarly complicated by symmetrical ether and alkene product formation.

Previous studies have indicated that silicon-hydrogen bond breaking is not extensive in the transition state for hydride transfer.<sup>9,10,20</sup> The approach of organosilanes to the carbonyl group, therefore, should not be as sensitive to steric repulsions from substituents of the carbonyl compound as would be reagents for which closer approach occurs in the transition state. In addition, however, in the four-center mechanism the carbonyl oxygen is involved in the hydride transfer step, forming a bond to silicon as the hydride is released. This demands that the silicon atom be bent toward the carbonyl oxygen in the transition state (structure A). In contrast, metal hydride reductions are



usually described by collinear C-H bond formation and M-H bond cleavage (structure B),<sup>21</sup> although such a geometry is not demanded (structure C).



Table II Comparative Stereoselectivities of Bulky Boron and Silicon Hydrides

	Relative yield, % cyclohexanol				
Reducing agent	<i>cis</i> -4- <i>tert</i> - Butyl	<i>cis</i> -4- Methyl	<i>cis</i> -2- Methyl-	trans- 3,3,5- Trimethyl	
Et,SiH <sup>2</sup>	32	36	48	84	
IPC, BHa, 22	37	33	94		
LiPBPH <sup>b,23</sup>	54	52	97	99	
sec-Bu <sub>2</sub> SiH <sup>2</sup>	55	58	64	96	
(t-Bu), SiH, <sup>ia</sup>	69	68	76	89	
$(t-Bu)_{1}^{2}$ MeSiH <sup>1a</sup>	72	67	74	99	
Li-sec-Bu <sub>3</sub> BH, 0° <sup>24</sup>	93	80	99	99.8	

<sup>a</sup> Diisopinocampheylborane. <sup>b</sup> Lithium perhydro-9bboraphenalylhydride.

In reductions of substituted cyclohexanones, groups bonded to the metal will be significantly more sensitive to steric effects from axial 3,5 positions in the transition state described by structure B than in that described by structure C. Since the transition state geometry in reductions by hindered organosilanes parallels C rather than B, the stereoselectivities in silane reductions should provide a reasonable model for the transition state geometries of other structurally comparable reducing agents.

The relative yields of the less stable isomers from reductions of alkyl-substituted cyclohexanones by selected bulky boron and silicon hydrides are given in Table II. By comparison with the results from 4-*tert*-butylcyclohexanone or 4-methylcyclohexanone, the yields of the less stable alcohols from reductions of 2-methylcyclohexanone and 3,3,5trimethylcyclohexanone by the alkyl borohydrides and diisopinocampheylborane are enhanced relative to those by the organosilanes. This difference in the sensitivities to axial 3-methyl and 2-methyl substituents is attributable to differences in the geometries of the reducing agents in the transition state for hydride transfer. The results for the boron hydrides in Table II are consistent with hydride transfer through a geometry resembling B rather than C.

## **Experimental Section**

General. Instrumentation has been previously described.<sup>2</sup> A Varian Model 485 digital integrator was used to determine peak areas in GLC analyses; reported yields were calculated with the use of experimentally determined thermal conductivity ratios. Cyclohexyl triethylsilyl ether and 4-*tert*-butylcyclohexyl triethylsilyl ether were prepared from the respective alcohols and triethylsilyl chloride in dry pyridine. Organosilanes were obtained commercially or were prepared as previously described.<sup>25</sup>

**Triethylsilyl Trifluoroacetate.** Triethylsilane (15.0 g, 0.13 mol) was added to a stirred solution of trifluoroacetic acid (29.4 g, 0.26 mol) and trifluoroacetic anhydride (3 ml), causing an immediate exothermic reaction. After 72 hr no triethylsilane was detected. Distillation at 17 Torr through a 17-cm Vigreux column yielded 52% of triethylsilyl trifluoroacetate, bp 61-66° [lit.<sup>26</sup> bp 153° (760 Torr)]. Even at the low temperature used for distillation hexaethyldisloxane was formed in measureable quantities; redistillation through a short-path column gave triethylsilyl trifluoroacetate which was >99% pure by GLC analysis.

Equilibrium Measurements. Stirred solutions of trifluoroacetic acid and cyclohexyl triethylsilyl ether or of trifluoroacetic acid, cyclohexanol, and triethylsilyl trifluoroacetate were analyzed by GLC at various times. Reactions using 1 and 10 equiv of trifluoroacetic acid (based on cyclohexyl triethylsilyl ether or equivalent amounts of cyclohexanol and triethylsilyl trifluoroacetate) were performed at 25°. Samples were quenched with excess saturated aqueous sodium bicarbonate and extracted twice with ether. (Control experiments showed that triethylsilyl trifluoroacetate was converted quantitatively to triethylsilanol by aqueous bicarbonate and that the silyl ether and cyclohexyl trifluoroacetate were not hydrolyzed during the work-up procedure.) The combined ether

extract was dried over anhydrous magnesium sulfate and filtered. and the ether was evaporated under reduced pressure. In a typical run samples were removed at 25 sec, 1, 5, 10, and 30 min. The equilibrium ratio from eq 6 was constant until cyclohexyl trifluoroacetate had begun to form (>10 min when 1 equiv of trifluoroacetic acid was used: 3 min when 10 equiv of acid was employed). When 1 equiv of trifluoroacetic acid was used the equilibrium ratio was attained at 5 min; equilibrium was achieved prior to the removal of the first sample (<30 sec) when 10 equiv of trifluoroacetic acid was employed.

Triethylsilane Reduction of Cyclohexanone, Product Analysis with Time. Trifluoroacetic acid (17.8 mmol) was added to a stirred solution of cyclohexanone (34.3 mmol), triethylsilane (33.5 mmol), and two GLC standards, phenylcyclohexane and 1-octyl ether. Aliquots were removed at intervals and quenched with excess "Tri-Šil", hexamethyldisilazane, trimethylchlorosilane in pyridine. This quenching procedure was used to enhance GLC separation of reaction components and to provide symmetrical peaks for analysis. Control experiments showed that cyclohexyl triethylsilyl ether and cyclohexyl trifluoroacetate were not affected by the quenching procedure and that cyclohexanol was quantitatively converted to the trimethylsilyl derivative. Quenched samples were stored in a freezer prior to analysis. At reaction times between 5 min and 6 hr GLC analysis gave product yields which corresponded to the equilibrium value for eq 6. Similar results were obtained using a quenching procedure similar to that described for the equilibrium studies, but analyses were significantly more difficult owing to unsymmetrical and overlapping peaks. For the aliquot removed at 250 sec the product ratio was determined to be 0.4; however, at this and shorter reaction times GLC peaks having similar areas to those of the reaction components (~0.2 mmol) and retention times overlapping with cyclohexyl trimethylsilyl ether interfered with the silyl ether and prevented an accurate determination of this compound. At no time was the level of cyclohexyl triethylsilyl ether greater than that of the trimethylsilyl derivative of cyclohexanol.

Di-tert-butylmethylsilanol and Di-tert-butylmethylsilyl Trifluoroacetate. Di-tert-butylmethylsilanol was prepared by the di-tert-butylmethylsilane reduction of acetone. The reaction mixture was quenched with excess 3 N sodium hydroxide, refluxed under the basic conditions for 24 hr, cooled, and extracted three times with pentane. The combined pentane extract was washed three times with water, dried over anhydrous magnesium sulfate, and filtered, and the pentane was evaporated under reduced pressure. The resulting solid was sublimed at 0.2 Torr to give a waxy white solid, mp 45-48° (46.5-48.5° after GLC purification), in 62% yield: ir (film) 3480 (broad, O-H), 1380, 1360 (t-Bu), 1250, and 800 cm<sup>-1</sup>; <sup>1</sup>H NMR (CCl<sub>4</sub>)  $\delta$  1.24 (s, 1 H, OH), 1.02 (s, 18 H, t-Bu), and 0.03 (s, 3 H, CH<sub>3</sub>).

Anal. Calcd for C9H22SiO: C, 62.00; H, 12.72; Si, 16.11. Found: C, 62.18; H, 12.71; Si, 16.24.

Trifluoroacetolysis of di-tert-butylmethylsilanol with trifluoroacetic anhydride gave di-tert-butylmethylsilyl trifluoroacetate: ir (film), 1780, 1470, 1390, 1365 and 820 cm<sup>-1</sup>; <sup>1</sup>H NMR (CCl<sub>4</sub>) δ 1.09 (s, 18 H) and 0.42 (s, 3 H).

Anal. Calcd for C<sub>11</sub>H<sub>21</sub>F<sub>3</sub>O<sub>2</sub>Si: C, 48.87; H, 7.83; Si, 10.39. Found: C, 49.02; H, 7.93; Si, 10.19.

Cyclohexanone Reductions by Di-tert-butylmethylsilane. Product Analyses. Reductions of 4-tert-butylcyclohexanone and 4-methylcyclohexanone were run as previously described.<sup>2</sup> Alkene, alcohol, trifluoroacetate, and silyl ether products were identified by <sup>1</sup>H NMR and GLC methods through comparison with authentic samples. For the reduction of 4-tert-butylcyclohexanone in the presence of trans-4-methylcyclohexanol, ketone (3.0 mmol), ditert-butylmethylsilane (3.2 mmol), and alcohol (2.5 mmol) were weighed into a round-bottom flask and 8.7 mmol of trifluoroacetic acid was added. The homogeneous solution was stirred at room temperature, and aliquots were removed at various times over a 3-hr period. Concurrently, 4-methylcyclohexanone (2.8 mmol) was reduced by di-tert-butylmethylsilane (3.2 mmol) in trifluoroacetic acid (8.7 mmol), and aliquots were removed at reaction times comparable to those for the 4-tert-butylcyclohexanone reduction. The

isomeric 4-methylcyclohexyl di-tert-butylsilyl ethers were identified by <sup>1</sup>H NMR ( $\delta$  3.95 and 3.35 for the methine hydrogen of the cis and trans isomers, respectively) and GLC methods. No trace of the 4-methylcyclohexyl silyl ethers (<0.5% of the 4-tert-butylcyclohexyl silyl ether) was observed during the 3-hr reaction period for the reduction of 4-tert-butylcyclohexanone. Although trans-4methylcyclohexanol was slowly converted to the corresponding trifluoroacetate, the amount of this alcohol present during the reduction of 4-tert-butylcyclohexanone was always greater than that of 4-tert-butylcyclohexanol.

Registry No.—cis-ROSiMe(t-Bu)<sub>2</sub>, 56889-82-8; trans-ROSi-Me(t-Bu)<sub>2</sub>, 56889-83-9; cis-RO<sub>2</sub>CCF<sub>3</sub>, 7556-86-7; trans-RO<sub>2</sub>CCF<sub>3</sub>, 7600-15-9; di-tert-butylmethylsilanol, 56889-84-0; di-tert-butylmethylsilyl trifluoroacetate, 56889-85-1.

#### **References and Notes**

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