none was reduced by triethylsilane in the presence of a 6 molar equiv excess of 4-*tert*-butylcyclohexanol (26% cis, 75% trans) under reaction conditions similar to those reported in Table VI. Analysis of the reaction products after complete reduction (IIa, 73%, IIIa, 27%) showed that, within experimental error, no discrimination between IIa and IIIa had occurred in the formation of *cis*-VIa and *trans*-VIa. The observed relative yields of ether products, 24% *trans,trans*-, 52% *cis,trans*-, and 24% *cis,cis*-4-*tert*-butylcyclohexyl ethers, could be predicted within experimental error from the data for triethylsilane (6.7 equiv CF_3COOH reaction) in Table VI.

(29) The reduction of 3,3,5-trimethylcyclohexanone by triethylsilane provides the only exception to these generalizations. The symmetrical ethers, 67% *trans,trans*-, 23% *cis,trans*-, and 10% *cis,cis*-3,3,5-trimethylcyclohexyl ethers, constituted 16% of the reduction products. Using the observed isomeric ratio, IIIe/IIe = 6.2, the relative rates for hydride transfer were k_{tt}/k_{tc} = 3.5 and k_{ct}/k_{cc} = 0.40, significantly less than the ratio of IIIe to IIe.

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Silane Reductions in Acidic Media. V. Reductions of Alkyl-Substituted Cyclohexanones by Di- and Tri-*tert*-butylsilanes. Steric Hindrance to Nucleophilic Attack at Silicon in the Trifluoroacetolysis of Silyl Alkyl Ethers[1a,b]

Michael P. Doyle*[1c] and Charles T. West

Department of Chemistry, Hope College, Holland, Michigan 49423

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Results are reported for the reductions of alkyl-substituted cyclohexanones by di-*tert*-butylsilane, di-*tert*-butylmethylsilane, and tri-*tert*-butylsilane in trifluoroacetic acid. The reactivities of di- and tri-*tert*-butylsilanes reflect the steric bulk of the *tert*-butyl groups. However, the inductive effect of alkyl substituents is pronounced; tri-*tert*-butylsilane reacts faster than di-*tert*-butylsilane in reductions of cyclohexanones. The thermodynamically less stable isomers are formed predominantly in *tert*-butylsilane reductions of cyclic ketones with remote substituents. However, silyl alkyl ethers formed in these reductions undergo trans elimination of silanol in competition with nucleophilic displacement at silicon. The relative rate for elimination increases with the increased steric bulk of alkyl groups bonded to silicon.

The reactivities of organosilicon compounds are strongly influenced by the steric bulk of *tert*-butyl substituents.[2-4] The *tert*-butyl group shields silicon from nucleophilic reagents that normally attack silicon.[4a] This steric effect should also be evident in the relative rates for reduction of ketones by *tert*-butylsilanes and in the stereoselectivities of these reductions. Indeed, in reductions of alkyl-substituted cyclohexanones di-*tert*-butylsilane is observed to be approximately 100 times less reactive than tri-*sec*-butylsilane.[1a]

Silyl alkyl ethers have been observed previously in organosilane reductions of carbonyl compounds when limited amounts of Bronsted acids are employed, and are presumed intermediates in these reactions.[5] Such compounds, which have proven to be highly useful in protecting the alcohol functional group in synthetic transformations,[6] are quantitatively solvolyzed in acidic media to alcohols. Alkoxy-*tert*-butyldimethylsilanes,[6c] although significantly more stable toward solvolysis, also react quantitatively with nucleophilic reagents to form alcohols. Nucleophilic attack at silicon in silyl alkyl ethers occurs in preference to attack at carbon. However, when silicon is shielded by more than one bulky *tert*-butyl group the rate of nucleophilic substitution at silicon may be sufficiently low so as to allow alternate pathways to become dominant.

In this paper we wish to report that highly hindered di- and tri-*tert*-butylsilanes do undergo selective hydride transfer reactions with alkyl-substituted cyclohexanones but that these reactions are complex owing to reactions caused by the shielding of silicon by *tert*-butyl groups. A novel elimination reaction of di- and tri-*tert*-butylsilyl alkyl ethers occurs in these reactions in competition with nucleophilic substitution at silicon.

Results

Di-*tert*-butylmethylsilane. The reactions of alkyl-substituted cyclohexanones with di-*tert*-butylmethylsilane are significantly and unexpectedly faster than those with di-*tert*-butylsilane. Using 6.6 equiv of trifluoroacetic acid, reductions of 4-*tert*-butyl, 4-methyl-, 2-methyl-, and even 3,3,5-trimethylcyclohexanone are complete within 20 hr at room temperature. Di-*tert*-butylmethylsilane is 20 to 40 times more reactive than di-*tert*-butylsilane in these reactions.

In Table I product yields from reductions of alkyl-substituted cyclohexanones by di-*tert*-butylmethylsilane are presented and compared to those from reductions by di-*tert*-butylsilane under the same reaction conditions. Only cycloalkene and cyclohexyl trifluoroacetate products are observed at 20 hr in reductions of alkylcyclohexanones by di-*tert*-butylmethylsilane when 6.6 equiv of trifluoroacetic acid is used. Cycloalkene formation is significant when di-*tert*-butylmethylsilane is employed under these reaction conditions and occurs to a greater extent than in reductions by di-*tert*-butylsilane. The relatively high yield of olefinic products in these reactions is surprising since under the same reaction conditions elimination processes are minimal (<1%) when less bulky silane reducing agents are used.[1a]

To determine the source of elimination processes in ketone reductions, lower acid concentrations were employed in order to decrease the rate of reduction and of solvolysis of the presumed silyl ether intermediates. Prior determinations had shown that alcohol, alkyl ether, and trifluoroacetate reaction products could not be the source of the alkenes formed in reductions by *tert*-butylsilanes. 4-*tert*-Butylcyclohexanone was treated with di-*tert*-butylmeth-

Table I
Di-*tert*-butylmethylsilane and Di-*tert*-butylsilane Reductions of Alkylcyclohexanones

Registry no.	Alkycyclohexanone	% yield from $(t\text{-Bu})_2MeSiH$[a,b] % cyclo-alkene[d]	% trifluoro-acetate	Rel % *cis*-trifluoro-acetate	% yield from $(t\text{-Bu})_2SiH_2$[b,c] % cyclo-alkene[d]	% trifluoro-acetate	Rel % *cis*-trifluoro-acetate
98-53-3	4-*tert*-Butyl-	13[g]	87	67	3	97	68
589-92-4	4-Methyl-	5	95	65	3	97	67
583-60-8	2-Methyl-	60[e,h]	40	35	30[f]	70	66
873-94-9	3,3,5-Trimethyl-	40[i]	60	<1	0	100	11

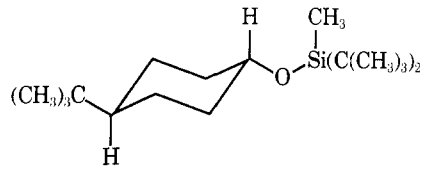
[a] Reductions were run at room temperature with 1.5 mmol of ketone, 1.5 mmol of silane, and 9.9 mmol of trifluoroacetic acid. Reaction times were 20 hr. Reduction of 4-*tert*-butylcyclohexanone was complete within 2 hr at room temperature. [b] No reaction products other than alkenes and trifluoroacetates were observed. [c] Reaction times for complete reduction varied from 72 hr (4-methylcyclohexanone) to more than 300 hr (2-methyl- and 3,3,5-trimethylcyclohexanone). [d] Absolute yield. [e] Sum of methylcyclohexane and 1-methylcyclohexyl trifluoroacetate. [f] Analyzed as methylcyclohexane; no 1-methylcyclohexyl trifluoroacetate was observed. [g] Registry no., 2228-98-0. [h] Registry no., 591-49-1. [i] Registry no., 503-45-7.

Table II
Di-*tert*-butylmethylsilane Reduction of 4-*tert*-Butylcyclohexanone[a]

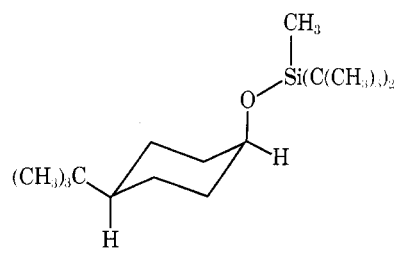
Time, hr	Relative yield, %[b] *cis*-I (56889-82-8)	*trans*-I (56889-83-9)	*cis*-II + *cis*-IV	*trans*-II + *trans*-IV	III	Σ *cis*-I, II, IV, + III
0.6	70	27	1.8	0.5	0.7	72.5
21	41	18	27	7	6	74
46	28	10	38	16	8	74
96	27	8	39	20	8	73

[a] Reduction was run at room temperature with 3.0 mmol of 4-*tert*-butylcyclohexanone, 3.5 mmol of di-*tert*-butylmethylsilane, and 9.0 mmol of trifluoroacetic acid and was complete within 3 hr. [b] Product yields based on GLC analyses and consistent with those obtained by ^1H NMR analyses at 15, 105, and 270 min and at 96 hr. Corrections have been made for the amounts of addition products from trifluoroacetolysis of III; at 96 hr the yield of 3-*tert*-butylcyclohexyl trifluoroacetates was 3%.

ylsilane at room temperature in the presence of 1.0, 1.5, and 3.0 equiv of trifluoroacetic acid, and these reactions were followed with time. The isomeric 4-*tert*-butylcyclohexyl di-*tert*-butylmethylsilyl ethers (I) and 4-*tert*-butyl-



trans-I



cis-I

cyclohexanols (II) were observed in addition to 4-*tert*-butylcyclohexene (III) and the isomeric 4-*tert*-butylcyclohexyl trifluoroacetates (IV). Typical results are given in Table II for the reduction in which 3.0 equiv of trifluoroacetic acid was used. The silyl ethers, *cis*- and *trans*-I, are, by far, the predominant reduction products from these reactions; subsequent transformations of the silyl ethers yield the trifluoroacetate and alkene products observed in organosilane reductions of ketones in trifluoroacetic acid media (Table I).

The stereoselectivity in the reduction of 4-*tert*-butylcyclohexanone by di-*tert*-butylmethylsilane should be constant with time.[7] However, from Table II the observed sum of cis products (*cis*-I + *cis*-II + *cis*-IV) decreases with increasing time, but the sum of the relative yields of *cis*-I, *cis*-II, III, and *cis*-IV is constant within experimental error throughout the 96-hr period during which the reaction products were analyzed. These results, which were confirmed by similar comparisons for reductions run with 1.0 equiv of trifluoroacetic acid, indicate that 4-*tert*-butylcyclohexene is formed specifically from *cis*-I.

Table III
Stereoselectivities in Cyclohexanone Reductions by Di-*tert*-butylsilane and Di-*tert*-butylmethylsilane in Trifluoroacetic Acid[a]

Alkylcyclohexanone	% less stable isomer[b] $(t\text{-Bu})_2MeSiH$	$(t\text{-Bu})_2SiH_2$
4-*tert*-Butyl	72	69
4-Methyl-	67	68
2-Methyl-	74	76
3,3,5-Trimethyl-	>99	89[c]

[a] Calculated by assuming that olefin products result solely from diaxial elimination of silyl cyclohexyl ethers. [b] From the data in Table I. [c] Although alkene products were not observed in this reaction, olefin formation with subsequent addition of trifluoroacetic acid may have occurred during the long reaction time required for complete reduction. Such a process might explain the unexpectedly low selectivity in this reduction.

The yield of 4-*tert*-butylcyclohexene was sensitive to both the concentration of acid, ranging from 13% (6.6 equiv of CF_3CO_2H) to 6% (1.0 equiv of CF_3CO_2H), and to the reaction temperature, 11% at 25° and 4% at −40° (3.0 equiv of CF_3CO_2H). However, the stereoselectivity in forming *cis*-4-*tert*-butylcyclohexyl products, calculated by assuming that 4-*tert*-butylcyclohexene is formed solely from *cis*-I, did not change over the range of reaction conditions employed and averaged 72 ± 1%. Similar calculations permit an estimate of the stereoselectivities in reductions of other

Table IV
Trifluoroacetolysis of 4-*tert*-Butylcyclohexene

CF_3CO_2H/4-*tert*-butylcyclohexene	Temp, °C	Yield, %[a] *trans*-V (31003-52-8)	*cis*-V (31003-51-7)	*cis*-IV (7556-86-7)	*trans*-IV (7600-15-9)	*trans*-V/*cis*-V	*cis*-IV/*trans*-IV	IV/V
20	25[b]	53	9	30	8	5.9	3.7	0.61
4.0	25[c]	50	9	31	10	5.6	3.1	0.70
2.0	80[b]	45	15	28	12	3.0	2.3	0.67

[a] Relative product yields based on ^1H NMR and GLC analyses. No products other than those reported were observed in significant yields. [b] Analyzed after 24 hr; 11% olefin remained unreacted. [c] Analyzed after 120-hr reaction time; 18% cycloalkene was unreacted.

Table V
Reduction of 4-*tert*-Butylcyclohexanone by Tri-*tert*-butylsilane[a,f]

Time, hr	% reduction[b]	Relative yield, %[c] VI	II[d]	III	*cis*-IV	*trans*-IV[e]	*trans*-V	*cis*-V[e]
21	50	64	9	5.5	10	8.0	3.0	0.5
27	53	57	10	7.4	12	9.3	3.7	0.6
93	85	51		22	13	9.0	4.2	0.8
264	94	20		50	13	9.3	6.5	1.2
720	97	10		38	21	10	18	3.0

[a] Reduction was run at room temperature with 2.5 mmol of 4-*tert*-butylcyclohexanone, 3.0 mmol of tri-*tert*-butylsilane, and 7.5 mmol of trifluoroacetic acid. [b] Based on tri-*tert*-butylsilane. [c] Product yields based on ^1H NMR analyses. GLC analyses of the quenched reaction solutions gave results which agreed substantially with the ^1H NMR data. Yields obtained at 145, 436, and 693 hr reaction time were in agreement with trends observed at reaction times reported here. [d] Only *cis*-II was observed. The relative yield of *trans*-II was not determined. [e] ^1H NMR analysis was used to give the sum of *trans*-IV and *cis*-V. The yields of the individual products were calculated using the *trans*-V/*cis*-V ratio in Table IV. [f] Registry no., 18159-55-2.

alkyl-substituted cyclohexanones. These calculations are given for both di-*tert*-butylsilane and di-*tert*-butylmethylsilane in Table III.

In the reduction of 2-methylcyclohexanone by di-*tert*-butylmethylsilane the elimination process from the cis alkyl silyl ether yielding 1-methylcyclohexene is dominant (60%); subsequent trifluoroacetolysis and ionic hydrogenation[8] of the 1-methylcyclohexene gives 1-methylcyclohexyl trifluoroacetate (23%) and methylcyclohexane (37%), respectively.[9] Neither 3-methylcyclohexene nor the 3-methylcyclohexyl trifluoroacetates were detected. Di-*tert*-butylmethylsilanol, di-*tert*-butylmethylsilyl trifluoroacetate, and the 2-methylcyclohexyl di-*tert*-butylmethylsilyl ethers are the only silane products.

Trifluoroacetolysis of 4-*tert*-Butylcyclohexene. Since olefin production is significant in reductions of 4-*tert*-butylcyclohexanone by *tert*-butylsilanes in trifluoroacetic acid, the selectivities of the addition of trifluoroacetic acid to 4-*tert*-butylcyclohexene were investigated. No previous study of the trifluoroacetolysis of alkylcyclohexenes has been reported; and, consequently, the stereoselectivities of trifluoroacetate products observed in silane reductions could be thought to reflect the stereoselectivities of the products from trifluoroacetolysis of alkyl-substituted cyclohexenes.

Trifluoroacetolysis of 4-*tert*-butylcyclohexene produces the geometrical isomers of both 3-*tert*-butylcyclohexyl trifluoroacetate (V) and the 4-*tert*-butylcyclohexyl trifluoroacetate (IV). The yields of these products under conditions comparable to those used in reductions of 4-*tert*-butylcyclohexanone are given in Table IV. Addition preferentially occurs to give V, and axial-trifluoroacetate products are favored over equatorial-substituted trifluoroacetates. The ratio of the yields of IV to V are not affected within experimental limits either by changes in the concentration of trifluoroacetic acid or by changes in temperature. The cis to trans ratio of V and IV, however, does reflect changes in temperature but not changes in trifluoroacetic acid concentration.

The low yield of 3-*tert*-butylcyclohexyl trifluoroacetate products in reductions of 4-*tert*-butylcyclohexanone by either di-*tert*-butylsilane or di-*tert*-butylmethylsilane under reaction conditions reported earlier indicates that trifluoroacetic acid addition to 4-*tert*-butylcyclohexene is not an important process in 4-*tert*-butylcyclohexyl trifluoroacetate production. This is further substantiated by the results from the reduction of 4-*tert*-butylcyclohexanone by di-*tert*-butylmethylsilane using 3 equiv of trifluoroacetic acid; the yield of 3-*tert*-butylcyclohexyl trifluoroacetate, after a reaction time of 96 hr, is only 3% (Table II).

Tri-*tert*-butylsilane. Among the *tert*-butylsilanes silicon is shielded to the greatest extent in tri-*tert*-butylsilane.[4a] Yet nearly complete reduction of 4-*tert*-butylcyclohexanone (>95%) by this highly hindered silane occurs within 95 hr at room temperature when 4 equiv of trifluoroacetic acid is employed. The rate of hydride transfer from tri-*tert*-butylsilane is greater than that from di-*tert*-butylsilane. The reaction products, however, are composed almost solely of 4-*tert*-butylcyclohexene (31%) and the 3- and 4-*tert*-butylcyclohexyl trifluoroacetates (64%), indicating that the elimination process, observed as a competing reaction in reductions by the di-*tert*-butylsilanes, is the dominant reaction in reductions by tri-*tert*-butylsilane.

The yields of products from the reduction of 4-*tert*-butylcyclohexanone by tri-*tert*-butylsilane using 3 equiv of trifluoroacetic acid were obtained by ^1H NMR and GLC analyses of the reaction mixture at various times and are reported in Table V. Relatively low yields of 4-*tert*-butylcyclohexanol (~5%) were observed at reaction times of less than 30 hr (~50% reduction); at longer reaction times this alcohol could not be detected. The isomeric 4-*tert*-butylcyclohexyl tri-*tert*-butylsilyl ethers (VI) were predominant initially (<100 hr) but were slowly converted to 4-*tert*-butylcyclohexene and to trifluoroacetate products. The rel-

ative yields of *cis*-VI at 21, 93, 168, and 720 hr were 96, 95, 94, and 73%, respectively, indicating that the rate of solvolysis of *cis*-VI is comparable to that of *trans*-VI.

Trifluoroacetolysis of 4-*tert*-butylcyclohexene accounts for the production of 3-*tert*-butylcyclohexyl trifluoroacetate (V) and for a fraction of the 4-*tert*-butylcyclohexyl trifluoroacetate (IV) obtained in the reduction process. Using the product ratios from Table IV for IV/V and for *cis*-IV/*trans*-IV the relative yields of the isomeric 4-*tert*-butylcyclohexyl trifluoroacetates resulting from trifluoroacetolysis of 4-*tert*-butylcyclohexene can be calculated and substracted from the observed values given in Table V. Using this method the relative yields of *cis*-IV (9.2 ± 1.7%) and *trans*-IV (7.6 ± 1.5%) are found to be relatively constant over the 720 hr reaction period; no trend is detectable. The yield of *trans*-IV is identical, within experimental error, with that of *trans*-VI (4–6%), indicating that under the reaction conditions employed *trans*-VI is converted solely to *trans*-IV and does not undergo elimination to 4-*tert*-butylcyclohexene. Similar results were obtained when 4-*tert*-butylcyclohexanone was treated with tri-*tert*-butylsilane at room temperature using 4.0 and 2.0 equiv of trifluoroacetic acid and at 80° using 2.0 equiv of trifluoroacetic acid.

Tri-*tert*-butylsilane reductions were run at −30° in an attempt to minimize olefin formation. Using 4 equiv of trifluoroacetic acid the silane reduction of 4-*tert*-butylcyclohexanone gave after 2 months reaction time 71% VI (97% cis), 23% IV (65% cis), and 6% III. The sum of the yields of *cis*-VI and those products resulting from *cis*-VI, *cis*-IV, and III was 90%. Similarly, the tri-*tert*-butylsilane reduction of 4-methylcyclohexanone under comparable conditions gave 78% 4-methylcyclohexyl tri-*tert*-butylsilyl ether (93% cis), 20% 4-methylcyclohexyl trifluoroacetate (65% cis), and 2% 4-methylcyclohexene (2 months reaction time). The sum of the yields of *cis*-VII and those products resulting from *cis*-VII, *cis*-4-methylcyclohexyl trifluoroacetate and 4-methylcyclohexene, was 88%. The major silicon product from these reductions was tri-*tert*-butylsilanol.

Attempts to displace the tri-*tert*-butylsilyl group from VI without elimination by alternative procedures were unsuccessful. The method successfully employed to remove the *tert*-butyldimethylsilyl protecting group did not affect VI even when significantly longer reaction times were used. Similarly, lithium aluminum hydride failed to reduce the tri-*tert*-butylsilyl ether even after heating at 55° for 4 days.

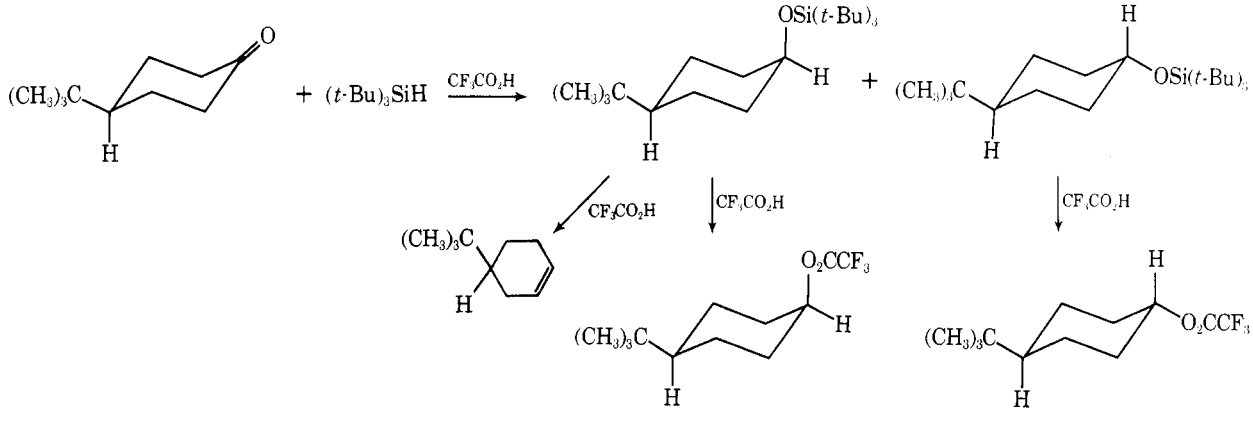
Discussion

Organosilane Reductions. The reactivities of di- and tri-*tert*-butylsilanes in ketone reductions reflect both the steric bulk of the *tert*-butyl group and the inductive effect of alkyl substituents. Qualitatively, the rates of cyclohexanone reductions by tri-*sec*-butylsilane are faster than those by di-*tert*-butylmethylsilane, which are greater than those by tri-*tert*-butylsilane. The rates for reductions by di-*tert*-butylsilane, however, are slower than those for similar reductions by tri-*tert*-butylsilane; *an increase in the number of alkyl substituents dramatically increases the reactivity of alkylsilanes in reduction processes.* An estimate of the relative reactivities of hindered organosilanes (given in parentheses) can be made through a comparison of reaction times for reduction: *sec*-Bu_3SiH (100), *t*-Bu_2MeSiH (30), *t*-Bu_3SiH (3), *t*-Bu_3SiH_2 (1).[10]

Reductions of alkyl-substituted cyclohexanones by di- and tri-*tert*-butylsilanes yield predominantly the less stable cyclohexyl derivative, either the cyclohexyl trifluoroacetate or silyl ether. The selectivity for the less stable isomer increases in the order *sec*-Bu_3SiH < $(t\text{-Bu})_2SiH_2$, $(t\text{-Bu})_2MeSiH$ < $(t\text{-Bu})_3SiH$. Indeed, the stereoselectivity for hydride transfer in tri-*tert*-butylsilane reductions of 4-*tert*-butylcyclohexanone (90% cis products) and 4-methylcyclohexanone (88% cis products) is similar to that achieved by either lithium tri-*sec*-butylborohydride[11] or lithium dimesitylborohydride bis(dimethoxyethane).[12] The usefulness of tri-*tert*-butylsilane in ketone reductions, however, is severely limited by the same factor which provides the exceptionally high degree of stereoselectivity in hydride transfer. The bulky *tert*-butyl groups not only provide steric hindrance to hydride transfer from the axial direction in cyclohexanone reductions but, also, effectively shield silicon from nucleophilic attack.

The dominant reaction pathway for silyl ethers produced in the reduction of 4-*tert*-butylcyclohexanone by tri-*tert*-butylsilane at or above room temperature is elimination. In this process elimination of the elements of tri-*tert*-butylsilanol occurs in acidic media only from *cis*-VI (Scheme I).

Scheme I



Reductions by di-*tert*-butylmethylsilane and, to a lesser extent, di-*tert*-butylsilane also occur with elimination competing with substitution at silicon.[13] The relative importance of the elimination reaction increases with an increase in the steric bulk about silicon. The relative rates for substitution at silicon (k_s) compared to those for elimination (k_e) can be determined from the ratios of *cis*-trifluoroacetate to alkene and are estimates for the shielding of silicon by *tert*-butyl groups. In reductions of 4-*tert*-butylcyclohexanone the ratios, k_s/k_e, from *cis*-4-*tert*-butylcyclohexyl silyl ethers are observed to be 22 for $(t\text{-Bu})_2SiH_2$, 4.5 for $(t\text{-Bu})_2MeSiH$, and 0.11 for $(t\text{-Bu})_3SiH$. For reductions of 2-methylcyclohexanone similar calculations of k_s/k_e for $(t\text{-Bu})_2SiH_2$ (1.5) and $(t\text{-Bu})_2MeSiH$ (0.23) show qualitative agreement with those from reductions of 4-*tert*-butylcyclo-

hexanone. Nucleophilic substitution is, therefore, highly sensitive to the steric environment about silicon, more so than are the rates for ketone reductions.

The observation of exclusive elimination from cis alkyl silyl ethers formed in silane reductions of 4-*tert*-butylcyclohexanone is consistent with a trans-elimination mechanism and implies that, if the chair cyclohexane conformer is assumed, the 4-*tert*-butyl group is conformationally larger than the $-OSiR_3$ substituent. In agreement with this prediction, the ^1H NMR spectrum of the isomeric mixture of 4-*tert*-butylcyclohexyl di-*tert*-butylmethylsilyl ethers (I) exhibits two proton absorptions for the $-Si(t\text{-}Bu)_2-$ groups with intensities expected from the relative amounts of axial- and equatorial-substituted isomers; only one signal for the 4-*tert*-butyl group is observed. The chemical shifts of the methine hydrogens (CHOSi) of I are δ 4.08 (*cis*-I) and 3.64 (*trans*-I), respectively, substantially the same as those from the isomeric 4-*tert*-butylcyclohexyl triethylsilyl ethers, δ 4.00 (cis isomer) and 3.57 (trans isomer). In contrast, the corresponding methine hydrogen of *cis*-VI absorbs at δ 4.37 and those of VII absorb at δ 4.33 (*cis*-VII) and 3.77 (*trans*-VII). The downfield shift for the methine hydrogen of tri-*tert*-butylsilyl ethers of alkylcyclohexanols can be explained by a long-range deshielding effect by the conformationally restricted tri-*tert*-butylsilyl group. Similar effects have been noted in other molecular systems.[14,15] However, molecular models of either VI or VII do not provide a clear distinction between the chair cyclohexane conformation and alternate conformations, and the observed chemical shift difference between VI or VII and I may be due to a change in ring conformation.

Trifluoroacetolysis of 4-*tert*-Butylcyclohexene. Although addition reactions have received considerable attention in the literature, there have been few studies of the stereochemical outcome of addition reactions and none of the addition of carboxylic acids to cycloalkenes. Trifluoroacetolysis of 4-*tert*-butylcyclohexene (III) produces the geometrical isomers of both 3- and 4-*tert*-butylcyclohexyl trifluoroacetates. The preference for the production of 3-*tert*-butylcyclohexyl trifluoroacetate (Table IV) indicates that the remote *tert*-butyl group plays a directive role in the addition process. The addition of diborane to III,[16] on the other hand, does not occur with a similar directive influence.

The influence of the *tert*-butyl group is also observed in the axial/equatorial trifluoroacetate ratios for IV (3.4 at 25°) and V (5.8 at 25°). Although the reason for the difference between these values is not obvious from our present results, the high axial/equatorial ratios are consistent with an ionic mechanism for addition in which the *tert*-butylcyclohexyl cations are preferentially trapped from the axial side. Similar selectivities are not observed in either the hydroboration[16] or epoxidation[18] reactions of III.

Experimental Section

General. Instrumentation has been previously described.[1a] 4-*tert*-Butylcyclohexene was synthesized from 4-*tert*-butylcyclohexyl methanesulfonate using standard procedures. The syntheses of *tert*-butylsilanes, the general reaction procedure, and product analyses are described elsewhere.[1a,4a]

Reductions of 4-*tert*-Butylcyclohexanone by Di-*tert*-butylmethylsilane. Product Analyses. Reactions were run as previously described.[1a] 4-*tert*-Butylcyclohexene and the isomeric 3- and 4-*tert*-butylcyclohexyl trifluoroacetates were identified by ^1H NMR and GLC methods. Product yields based on the integration of characteristic ^1H NMR absorptions were within 2% of those obtained by the integration of GLC peaks assigned to the same products.

For reductions using di-*tert*-butylmethylsilane, di-*tert*-butylmethylsilanol and di-*tert*-butylmethylsilyl trifluoroacetate were identified by ^1H NMR and GLC comparison with authentic samples. The GLC peaks assigned to the isomeric 4-*tert*-butylcyclohexyl di-*tert*-butylmethylsilyl ethers (I) were collected together and analyzed: viscous, colorless liquid; ^1H NMR ($CDCl_3$) δ 4.08 and 3.64 (m, 1 H, 81% *cis*-I and 19% *trans*-I, respectively), 2.13–1.17 (m, 9 H), 0.98 and 0.96 (two sharp singlets, 18 H, 80 and 20%, respectively), 0.86 (s, 9 H), and 0.3 (s, 3 H); ir (film) 2950, 2890, 1440 and 1375 (CH_3), 1390 and 1365 (*t*-Bu), 1245 and 797 ($SiCH_3$), 1110 (C–O), and 1050 cm^{-1} (Si–O–C); mass spectrum *m/e* (rel intensity) 257 (0.45) 256 (1.60), 255 (7.00), 215 (0.45), 214 (1.74), 213 (8.50), 75 (100), 57 (23).

Anal. Calcd for $C_{19}H_{40}OSi$: C, 73.00; H, 12.90; Si, 8.98. Found: C, 73.08; H, 12.83; Si, 9.02.

Reduction of 2-Methylcyclohexanone by Di-*tert*-butylmethylsilane. Product Analyses. Methylcyclohexane, 1- and 2-methylcyclohexyl trifluoroacetates, di-*tert*-butylmethylsilanol, and di-*tert*-butylmethylsilyl trifluoroacetate were analyzed by ^1H NMR and GLC comparison with authentic samples. The GLC peak assigned to the 2-methylcyclohexyl di-*tert*-butylmethylsilyl ethers was collected and analyzed: ^1H NMR (CCl_4) δ 3.33 (m, 11 H), 2.2–1.2 (m, 12 H), 1.0 and 0.97 (singlets, 18 H), and 0.04 (s, 3 H).

Addition of Trifluoroacetic Acid to 4-*tert*-Butylcyclohexene. The following illustrates the reaction procedure and method of analysis for the isomeric 3- and 4-*tert*-butylcyclohexyl trifluoroacetates. To 0.160 g (1.15 mmol) of 4-*tert*-butylcyclohexene was added 2.61 g (23.0 mmol) of trifluoroacetic acid with stirring at room temperature. The initially heterogeneous light-orange mixture became homogeneous upon continued stirring and slowly turned to a red-brown color after 24 hr. ^1H NMR analysis of the reaction mixture indicated four trifluoroacetate products: 50% *trans*-V (δ 5.57), 28% *cis*-IV (δ 5.43), and 22% of a mixture of *cis*-V and *trans*-IV (δ 5.08). The 4-*tert*-butylcyclohexyl trifluoroacetates (IV) were identified from their characteristic chemical shifts by comparison with authentic samples; the identities of the 3-*tert*-butylcyclohexyl trifluoroacetates were inferred.

The reaction mixture was quenched with 25 ml of saturated aqueous sodium bicarbonate, and the resulting mixture was extracted five times with 5-ml portions of pentane. The combined pentane extract was dried over anhydrous magnesium sulfate and filtered, the filter cake was washed several times with small portions of pentane, and the combined pentane washes and extract were concentrated under reduced pressure. GLC analysis on a 5-ft 15% SE-30 column at 130° gave peaks for the following compounds (retention times given in parentheses): unknown (3.8%, 4.1 min), III (11.2%, 4.9 min), *trans*-V (45.0%, 9.0 min), *cis*-IV (25.5%, 9.7 min), *cis*-V (7.7%, 10.4 min), and *trans*-IV (6.8%, 11.2 min). The assignments of III and *cis*- and *trans*-IV were made by retention time comparisons and peak enhancements with authentic samples. The assignments for *cis*- and *trans*-V were consistent with the observation that the less stable isomer eluted prior to the more stable equatorial isomer.[1a]

Analyses of the alcohols formed after saponification of the worked-up reaction mixture using 3 *N* aqueous sodium hydroxide confirmed the results obtained by ^1H NMR and GLC analyses of the trifluoroacetate mixture. The use of the shift reagent 2,2,6,6-tetramethyl-3,5-heptanedioneeuropium(III) [Eu(Thd)$_3$] provided a superior method for determining product yields from the complex mixture. Enough Eu(Thd)$_3$ was added to a ^1H NMR sample to completely separate *trans*-V-OH and *cis*-IV-OH CHOH absorptions (570 and 595 Hz, respectively, relative to internal Me_4Si). The *cis*-IV-OH isomer experienced a larger shift than did the *trans*-V-OH isomer; the differential shift was easily observed upon successive additions of small portions of the shift reagent to the sample. The relative proportions of *trans*-V-OH and *cis*-IV-OH were obtained by integration of the shifted absorptions: 62 and 38%, respectively (compared with 64% *trans*-V and 36% *cis*-IV by GLC analysis).

GLC analysis of the saponification mixture on a 5-ft 20% Carbowax 20M column programmed at 4°/min from 130 to 180° gave two alcohol peaks (84 and 16%, respectively) having the same retention times as *cis*-IV-OH and *trans*-IV-OH. Assuming that both axial alcohols (*cis*-IV-OH and *trans*-V-OH) have the same retention time and that both equatorial alcohols, likewise, have the same retention times, there is excellent agreement between these results and the GLC results for the trifluoroacetates (overall, 83% axial and 17% equatorial isomers).

Reduction of 4-*tert*-Butylcyclohexanone by Tri-*tert*-butylsilane. Product Analyses. To 0.38 g (2.5 mmol) of 4-*tert*-butylcyclohexanone and 0.60 g (3.0 mmol) of tri-*tert*-butylsilane was added 0.90 g (7.5 mmol) of trifluoroacetic acid at room tempera-

ture. The homogeneous light yellow reaction mixture was analyzed by ^1H NMR spectroscopy and GLC at various times, and the identities and yields of reaction products were determined. Products not identified by retention time comparison and peak enhancement with authentic samples were collected and analyzed.

Tri-*tert*-butylsilanol (82% yield) was identified spectroscopically: ^1H NMR (CCl_4) δ 1.42 (s, 1 H) and 1.12 (s, 27 H); ir (film) 3720, 3680 (weak, sharp) and 3460 cm^{-1} (broad, strong).

Tri-*tert*-butylsilyl trifluoroacetate (18% yield) was also detected: ^1H NMR (CCl_4) δ 1.21 (s); ir (film), 1775 cm^{-1} (C=O).

The *cis*- and *trans*-4-*tert*-butylcyclohexyl tri-*tert*-butylsilyl ethers were assigned to two peaks separable on a 5-ft 10% FFAP column. A mixture consisting of 97% of the cis isomer was collected as a white, crystaline solid: mp 91–92°; ^1H NMR ($CDCl_3$) δ 4.37 (m, 1 H), 2.23–1.33 (m, 9 H), 1.13 (s, 27 H), and 0.86 (s, 9 H); ir (film) 1385, 1360 and 1225 (*t*-Bu), 1110 (C–O), 1055 (SiOC), and 810 cm^{-1} (Si–C); mass spectrum *m/e* (rel intensity) 297 (M − 57, 0.40), 255 (1.5), 213 (5.3), 75 (100), 73 (14), 57 (38), 41 (22), 29 (26).

Anal. Calcd for $C_{22}H_{46}OSi$: C, 74.50; H, 13.07; Si, 7.92. Found: C, 74.20; H, 12.97; Si, 8.16.

Reduction of 4-Methylcyclohexanone by Tri-*tert*-butylsilane. Product Analyses. To 0.11 g (1.0 mmol) of 4-methylcyclohexanone and 0.30 g (1.5 mmol) of tri-*tert*-butylsilane was added 0.46 g (4.0 mmol) of trifluoroacetic acid at 0°. The homogeneous, light yellow solution was transferred to a freezer (−30°). After cooling a viscous, colorless liquid separated to the top of the reaction mixture. After 2 months ^1H NMR analysis indicated approximately 60% reduction. The reaction mixture was quenched with an excess of 3 *N* sodium hydroxide and worked up in the usual manner. Analysis by GLC showed one peak that could not be identified by comparison with authentic samples. The unidentified peak, which was homogeneous on Carbowax 20M, SE-30, and FFAP columns, was collected as a colorless, viscous liquid and analyzed as 4-methylcyclohexyl tri-*tert*-butylsilyl ether: ^1H NMR ($CDCl_3$) δ 4.33 and 3.77 (multiplets, 1 H), 2.2–1.2 (m, 9 H), 1.13 (s, 27 H), and 0.92 (broadened s, 3 H); ir (film) 1387, 1360 and 1230 (*t*-Bu), 1130 (C–O), 1055 (SiOC), and 810 cm^{-1} (Si–C); mass spectrum *m/e* (rel intensity) 257 (0.09), 256 (0.34), 255 (1.7), 215 (0.42), 214 (1.1), 213 (5.8), 173 (1.1), 172 (3.8), 171 (22), 75 (100), 73 (16), 57 (14), 55 (21), 45 (13), 41 (17), and 29 (10).

Anal. Calcd for $C_{19}H_{40}OSi$: C, 73.00; H, 12.90; Si, 8.98. Found: C, 72.87; H, 12.77; Si, 8.77.

Registry No.—*cis*-II, 937-05-3; *trans*-II, 937-06-4; *cis*-VI, 56889-86-2; *trans*-VI, 56889-87-3; $(t\text{-Bu})_2MeSiH$, 56310-20-4; $(t\text{-Bu})_2SiH_2$, 30736-07-3; *cis*-4-methylcyclohexyl trifluoroacetate, 31003-53-9; *trans*-4-methylcyclohexyl trifluoroacetate, 31003-54-0; *cis*-2-methylcyclohexyl trifluoroacetate, 31003-40-4; *trans*-2-methylcyclohexyl trifluoroacetate, 31003-41-5; *cis*-3,3,5-trimethylcyclohexyl trifluoroacetate, 56889-88-4; *trans*-3,3,5-trimethylcyclohexyl trifluoroacetate, 56889-89-5; *cis*-2-methylcyclohexyl di-*tert*-butylmethylsilyl ether, 31003-40-4; *trans*-2-methylcyclohexyl di-*tert*-butylmethylsilyl ether, 31003-41-5; tri-*tert*-butylsilanol, 56889-90-8; tri-*tert*-butylsilyl trifluoroacetate, 56889-91-9; 4-methylcyclohexyl tri-*tert*-butylsilyl ether, 56889-92-0.

References and Notes

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(9) Ionic hydrogenation of 1-methylcyclohexene by di-*tert*-butylmethylsilane is relatively slow compared to similar reactions using less hindered silanes. The reaction of 1-methylcyclohexene with an equimolar amount of di-*tert*-butylmethylsilane in 6 equiv of trifluoroacetic acid gives a mixture of methylcyclohexane (65%) and 1-methylcyclohexyl trifluoroacetate (35%) after 26 hr reaction time. The silane reaction products from this reaction, as well as from the reductions of alkylcyclohexanones, are di-*tert*-butylmethylsilyl trifluoroacetate and di-*tert*-butylmethylsilanol.

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