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SILANE REDUCTIONS IN ACIDIC MEDIA

VIII *. BORON TRIFLUORIDE CATALYZED ORGANOSILANE REDUCTIONS. SELECTIVITY AND MECHANISM

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Summary

Aldehydes and ketones are selectively reduced by organosilanes in boron trifluoride etherate through a process in which boron trifluoride is consumed and fluorosilanes are formed. Reductions of aldehydes and ketones by triethylsilane produce, after hydrolysis, alcohols and symmetrical ethers or, when aryl ketones are reduced, hydrocarbons. Two new synthetic transformations involving organosilanes, reductive elimination and acylation-reduction, are described. The mechanism of reduction in $BF_3 \cdot Et_2O$ is suggested to involve hydrosilylation of the boron trifluoride-activated carbonyl group followed by fluoride displacement at silicon. The stereoselectivity of the boron trifluoride catalyzed reduction in reactions with alkyl-substituted cyclohexanones is described and compared to similar transformations with other acid catalysts. The stereochemical data show that in hydride transfer reactions Lewis acid complexation with the carbonyl oxygen plays a major role in determining product selectivity.

Introduction

Reductions of organic compounds by organosilanes require activation of the carbon center by a suitable acid catalyst. The nature of the acid employed in these reactions influences the rate of reduction and, more importantly, the extent of reactions subsequent to the hydride transfer step [2]. In trifluoroacetic acid media, for example, hydrosilylation of the carbonyl group by hindered organosilanes yields relatively stable alkyl silyl ethers [3]; subsequent reactions of the alkyl silyl ether with trifluoroacetic acid give alcohol and silyl trifluoroaceta-

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* For Part VII, see ref. 1.

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te products. With less sterically encumbered organosilanes such as triethylsilane, however, reactions subsequent to hydrosilylation are rapid and the observed reaction products from aldehyde and ketone reductions are alkyl trifluoroacetates and silyl trifluoroacetates.

Although Lewis acid catalyzed reductions of carbonyl compounds by organosilanes have been less thoroughly investigated than those employing Brønsted acids, hydrosilylation is the principal result and subsequent reactions of alkyl silyl ethers with common Lewis acids are not observed [4—6]. Ketone reductions by triethylsilane employing catalytic amounts of anhydrous zinc chloride or aluminum chloride, for example, yield alkyl silyl ethers and, through a parallel competing process, symmetrical ethers. Rhodium(I) catalysts have more recently been investigated as hydrosilylation catalysts, principally to effect asymmetric reductions of prochiral ketones [7—10]; although the mechanism of these reductions is not known with certainty, the rhodium(I) catalyst does appear to act as a Lewis acid template for the reducible substrate.

In reductions by organosilanes the nature of the Lewis acid is expected to influence reaction selectivity as well as the stability of the hydrosilylation product. Metal fluoride catalysts, in particular, are of interest because of their pronounced ability to effect fluoride transfer to silicon derivatives [11—13] and their potential influence on the geometry of the transition state during the transfer of hydride from silicon to carbon in hydrosilylation reactions [3]. In this paper we report the stereochemistry and mechanism of organosilane reductions involving boron trifluoride.

Results and discussion

Organosilane reductions in boron trifluoride etherate

In contrast to hydrosilylation reactions catalyzed by metal chlorides, aldehydes and ketones are rapidly reduced at room temperature by triethylsilane in boron trifluoride etherate primarily to borate esters and symmetrical ethers. Triethylsilyl fluoride is the oxidation product. Product yields from reductions of representative carbonyl compounds after basic hydrolysis are presented in Table 1. Symmetrical ethers are formed preferentially in reactions with aldehydes and are less evident in ketone reductions; similar results were observed for triethylsilane reductions in trifluoroacetic acid [2]. Increasing the concentration of the acid also leads to a decrease in ether formation. However, increasing the amount of ethyl ether leads to an increase in the relative yield of symmetrical ether; for example, employing $BF_3 \cdot 2Et_2O$ in a molar amount equivalent to that of cyclohexanone results in a 39% yield of cyclohexyl ether, nearly three-times more than that obtained with $BF_3 \cdot Et_2O$ under similar conditions.

Boron trifluoride is consumed during the reaction of triethylsilane with carbonyl compounds. When less than one-third molar equivalent of boron trifluoride etherate is employed, reduction is incomplete; the extent of reaction corresponds to a stoichiometric requirement of one BF_3 to three $R_2C{=}O$ for both borate ester (eq. 1) and ether (eq. 2) formation.

$$3\ R_2C{=}O + 3\ Et_3SiH + BF_3 \rightarrow (R_2CHO)_3B + 3\ Et_3SiF \qquad (1)$$

$$6\ R_2C{=}O + 6\ Et_3SiH + 2\ BF_3 \rightarrow 3\ (R_2CH)_2O + 6\ Et_3SiF + B_2O_3 \qquad (2)$$

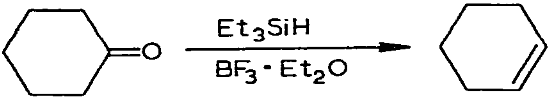
TABLE 1

PRODUCT YIELDS FROM ALDEHYDE AND KETONE REDUCTIONS BY TRIETHYLSILANE IN BORON TRIFLUORIDE ETHERATE [a]

$R_2C{=}O$	$[R_2CO]/[BF_3 \cdot Et_2O]$	Yield(%) [b]		
		R_2CHOH	$(R_2CH)_2O$	Alkene
Octanal	2.0	34	66	0
Benzaldehyde	2.0	25	75	
Cyclohexanone	3.0	65	30	5
	2.0	67	33	0
	1.0	86	14	0
	0.3	94	6	0

[a] Reactions were run at room temperature. A 10% molar excess of triethylsilane to carbonyl compound was used. [b] Relative yield of products.

Borate esters were inferred from ^1H NMR spectra of the reaction mixtures prior to basic hydrolysis but were not further identified. Attempts to isolate the borate reaction products from the reaction of cyclohexanone with triethylsilane in $BF_3 \cdot Et_2O$ by distillation led, instead, to cyclohexene which was recovered in 68% yield. The formation of cyclohexene by this procedure represents an unusual but facile one-pot reductive elimination (eq. 3).



(3)

Aryl ketones which were previously observed to undergo carbonyl group reduction to methylene in trifluoroacetic acid [14] were similarly reduced in boron trifluoride etherate. Thus acetophenone and benzophenone were quantitatively converted to ethylbenzene and diphenylmethane, respectively, by triethylsilane in $BF_3 \cdot Et_2O$. Carboxylic acids, amides, esters, and nitro compounds were unaffected by triethylsilane in $BF_3 \cdot Et_2O$ over time periods that were more than 100-times longer than those required for the reduction of aldehydes and ketones. Alkenes were similarly unreactive in this reducing medium, in contrast to their facile ionic hydrogenation in trifluoroacetic acid media [15].

Benzoyl chloride is not reduced by triethylsilane in $BF_3 \cdot Et_2O$. However, Friedel—Crafts acylation reactions are observed under similar reaction conditions with boron trifluoride catalysis [16], suggesting that the Friedel—Crafts acylation - silane reduction reactions can be combined in a one-step procedure for the alkylation of aromatic compounds without rearrangement (eq. 4). Indeed, the combination of benzoyl chloride with benzene and triethylsilane in

$$ArH + RCOCl \xrightarrow[BF_3 \cdot Et_2O]{Et_3SiH} ArCH_2R \qquad (4)$$

$BF_3 \cdot Et_2O$ does result in the production of diphenylmethane (30% yield).

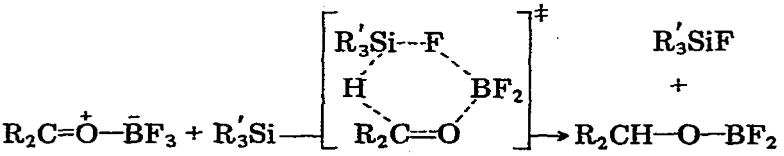
Mechanism of aldehyde and ketone reductions

The functional group selectivity of triethylsilane in boron trifluoride etherate as well as the nature of the reaction products in aldehyde and ketone reductions suggested that the reducing agent in these processes was the organosilane. That a boron hydride species is not involved in these reactions [17] was confirmed by IR analysis of triethylsilane in $BF_3 \cdot Et_2O$. No change in the intensity of the Si—H frequency (2100 cm^{-1}) was observed over a period comparable to that used for carbonyl group reductions, and no identifiable B—H bond absorption was detected.

Alkyl silyl ethers were not observed during or following reductions by triethylsilane in $BF_3 \cdot Et_2O$. In contrast, comparable analyses provided clear evidence for the intermediacy of alkyl silyl ethers during reductions in trifluoroacetic acid [2,3]. The possibility that these reaction intermediates are not formed in organosilane reductions that occur in boron trifluoride etherate must, therefore, be considered. Our analysis is limited to two mechanistic schemes; more complex pathways are not considered. In Scheme 1 hydrogen transfer from silicon to carbon and fluoride transfer from boron to silicon occur simultaneously through a six-center cyclic transition state. Retention of configuration is the expected result of this scheme. In Scheme 2 boron trifluoride serves to activate the carbonyl group for hydrosilylation in a four-center cyclic transition state; a subsequent rapid reaction of the alkyl silyl ether with boron trifluoride is proposed to yield the observed products. Since the formation of fluorosilanes from alkoxysilanes (eq. 8) is observed to occur with predominant inversion of configuration [11,18] and hydrosilylation (eq. 7) occurs with retention at silicon, the net stereochemical result at silicon from Scheme 2 is expected to be inversion of configuration.

SCHEME 1

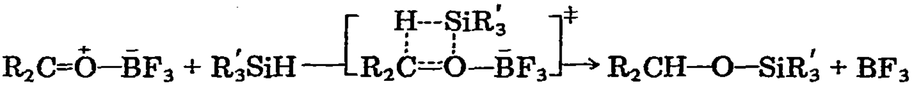
$$R_2C{=}O + BF_3 \rightleftharpoons R_2C{=}\overset{+}{O}{-}\overset{-}{B}F_3 \qquad (5)$$



$$R_2C{=}\overset{+}{O}{-}\overset{-}{B}F_3 + R'_3Si \longrightarrow \left[\begin{array}{ccc} R'_3Si & \cdots & F \\ H & & BF_2 \\ & R_2C{=}O & \end{array}\right]^{\ddagger} \longrightarrow \begin{array}{c} R'_3SiF \\ + \\ R_2CH{-}O{-}BF_2 \end{array} \qquad (6)$$

SCHEME 2

$$R_2C{=}O + BF_3 \rightleftharpoons R_2C{=}\overset{+}{O}{-}\overset{-}{B}F_3 \qquad (5)$$



$$R_2C{=}\overset{+}{O}{-}\overset{-}{B}F_3 + R'_3SiH \longrightarrow \left[\begin{array}{c} H\cdots SiR'_3 \\ R_2C{=}\overset{+}{O}{-}\overset{-}{B}F_3 \end{array}\right]^{\ddagger} \longrightarrow R_2CH{-}O{-}SiR'_3 + BF_3 \qquad (7)$$

$$R_2CH{-}O{-}SiR'_3 + BF_3 \longrightarrow R_2CH{-}O{-}BF_2 + R'_3SiF \qquad (8)$$

Reduction of acetone by (+)-α-naphthylphenylmethylsilane (abbreviated as (+)-R_3Si^*H) in boron trifluoride etherate gave (—)-α-naphthylphenylmethylfluorosilane in 11 ± 2% optical purity when the molar ratio of acetone to $BF_3 \cdot Et_2O$ was between 1.4 and 5. At molar ratios of acetone to $BF_3 \cdot Et_2O$ less than one only racemic α-naphthylphenylmethylfluorosilane was obtained. The net inversion of configuration in the production of the silyl fluoride from the silane is consistent with Scheme 2. However, the production of α-naphthylphenylmethylfluorosilane with 56% inversion from reductions of acetone in $BF_3 \cdot Et_2O$ contrasts with the 73% inversion from the reaction of (+)-$R_3Si^*OCH_3$ with $BF_3 \cdot Et_2O$ under similar reaction conditions [11b] and with the 70% inversion observed in the formation of α-naphthylphenylmethylfluorosilane after treatment of (+)-$R_3Si^*OC(CH_3)_3$ with $BF_3 \cdot Et_2O$ [11b]. The production of R_3SiF solely by Scheme 2 would have been expected to occur with at least 70% inversion of configuration at silicon (40% optical purity of R_3Si^*F).

The decreased yield of inverted product in reductions of acetone by (+)-R_3Si^*H may not be ascribed as the stereochemical consequence of competitive ether formation (eq. 2); no experimentally meaningful change in the optical purity of isolated α-naphthylphenylmethylfluorosilane was observed when reaction conditions that led to a substantial increase in the relative yield of symmetrical ether were employed. In addition, those reductions in which the molar ratio of acetone to $BF_3 \cdot Et_2O$ was less than one, reaction conditions that minimized symmetrical ether formation, resulted in only racemic α-naphthylphenylmethylfluorosilane.

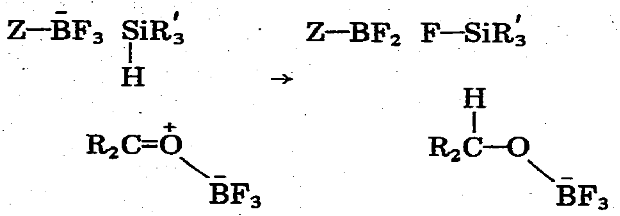
A commercial mixture of menthone and isomenthone was similarly reduced by (+)-α-naphthylphenylmethylsilane in $BF_3 \cdot Et_2O$. However, menthene was a major constituent of the reaction products and only racemic fluorosilane was recovered. In this case elimination competes with substitution presumably by a mechanism analogous to that previously used to explain olefin formation from reductions of alkyl-substituted cyclohexanones by hindered organosilanes in trifluoroacetic acid [19].

Hexachloroacetone and di-tert-butyl ketone were also treated with (+)-α-naphthylphenylmethylsilane in $BF_3 \cdot Et_2O$. However, reduction of these compounds was extremely slow; competing cleavage of the α-naphthyl group preceeded carbonyl group reduction. The formation of naphthalene and phenylmethylfluorosilane, which occurred slowly over a period of more than nine days at 50° C, is explained by hydrolytic cleavage of the reactant silane.

Scheme 2 requires the intermediacy of alkyl silyl ethers. Since these compounds are not detected during reduction, they must be converted to the fluorosilane at a faster rate than they are formed. Prior results from the reaction of (—)-α-naphthylphenylmethyl-(—)-menthoxysilane with boron trifluoride etherate have indicated that fluorosilane formation is relatively slow (5 h at 48° C) [11a]; however, complete reduction of an isomenthone/menthone mixture by α-naphthylphenylmethylsilane in $BF_3 \cdot Et_2O$ under comparable conditions is considerably slower, requiring more than 30 h. In addition, treatment of α-naphthylphenylmethylmethoxysilane with a molar excess of $BF_3 \cdot Et_2O$ yields the corresponding fluorosilane quantitatively within 10 min at room temperature, indicating by comparison with the menthoxy derivative that fluoride transfer from boron to silicon is subject to steric interference from alkyl groups remote from silicon. The same conclusion can be drawn by comparing R_3SiOCH_3 and $R_3SiOC(CH_3)_3$ in their reactions with $BF_3 \cdot Et_2O$ [11b].

The accumulation of data suggests that the mechanism of organosilane reductions of carbonyl compounds in $BF_3 \cdot Et_2O$ is primarily a two-step process which parallels that observed in reductions of ketones by hindered organosilanes in trifluoroacetic acid [3]. Hydrosilylation of the boron trifluoride-activated carbonyl group preceeds fluoride displacement at silicon (Scheme 2). However, alternate schemes for carbonyl group reductions by organosilanes in which fluoride transfer to silicon and hydrogen transfer to carbon occur simultaneously (Schemes 1 and 3) cannot be entirely dismissed.

SCHEME 3



In Scheme 3 fluoride transfer occurs from a boron fluoride not associated with the carbonyl compound that is being reduced; the stereochemical course of this process may parallel that observed in the reduction of trityl halides by R_3Si^*H [20] in methylene chloride, racemization, or the high inversion of configuration in the reaction of R_3Si^*H with silver tetrafluoroborate in ether [21]. Additional information is necessary to clarify the mechanism of carbonyl group reductions by relatively unhindered organosilanes.

Stereoselectivity in cyclic ketone reductions

Table 2 presents the relative yields of the less stable alcohol isomer from reductions of alkyl-substituted cyclohexanones by triethylsilane in $BF_3 \cdot Et_2O$ and compares these data to similar results from reductions in trifluoroacetic acid and

TABLE 2

STEREOSELECTIVITIES OF TRIETHYLSILANE REDUCTIONS OF ALKYL-SUBSTITUTED CYCLOHEXANONES

		Relative yield, (%) from reduction in		
Cyclohexanone	Alcohol product	BF · Et_2O [a]	CF_3COOH [b]	H_2SO_4 [b]
2-Methyl-	*cis*-2-Methyl-cyclohexanol	64	48	54
3-Methyl-	*trans*-3-Methyl-cyclohexanol	67	42	39
4-Methyl-	*cis*-4-Methyl-cyclohexanol	60	36	35
4-tert-Butyl-	*cis*-4-tert-Butyl-cyclohexanol	61	32	32
3,3,5-Trimethyl-	*trans*-3,3,5-Tri-methylcyclohexanol	95	84	90

[a] Reactions were run at room temperature. Alcohols were the only products observed after basic hydrolysis.
[b] Data taken from ref. 22.

aqueous sulfuric acid/ethyl ether media [22]. Use of a 3-fold molar excess of $BF_3 \cdot Et_2O$ over ketone, completely suppresses symmetrical ether formation in these reductions; by comparison, with a $[R_2C{=}O]/[BF_3 \cdot Et_2O]$ molar ratio of 3.0 for the triethylsilane reduction of 4-tert-butylcyclohexanone, 4-tert-butylcyclohexyl ether is produced in 42% yield (44% *cis, cis-*, 46% *cis, trans-*, and 10% *trans, trans-*). Elimination to cycloalkenes is not observed even from reactions of triethylsilane with 2-methylcyclohexanone in $BF_3 \cdot Et_2O$.

The yield of the less stable alcohol isomer is consistently greater from reductions by triethylsilane in $BF_3 \cdot Et_2O$ than from those in Bronsted acids. This increase in selectivity for hydride transfer from the equatorial direction is caused by the change in the Lewis acid. The effects of Lewis acids (or metal ions) on reactivity and selectivity in hydride transfer reactions have been generally overlooked. These results and those from other laboratories [23,24] provide an increasing amount of evidence that in hydride transfer reactions Lewis acid complexation with the carbonyl oxygen plays a major role in determining product selectivity.

Table 3 presents the stereochemical results from reductions of 4-tert-butylcyclohexanone by triethylsilane which employ selected acid catalysts. Compared with protonic acids, the use of Lewis acids generally leads to significantly higher relative yields of the less stable alcohol derivative. Indeed, by comparing the data in Table 3 it is evident that changing the steric bulk of the acid required to acti-

TABLE 3

ACID CATALYZED REDUCTIONS OF 4-TERT-BUTYLCYCLOHEXANONE BY TRIETHYLSILANE [a]

Acid	$[Acid]/[R_2C{=}O]$	Alcohol derivative [b]	Alcohol derivative (%)	Relative *cis*-isomer (%)	Symmetrical ether (%)
CF_3COOH [c]	6.8	Trifluoroacetate	83	32	17
$H_2SO_4.H_2O$ [c]	0.70	Alcohol	100	32	0
HCOOH	2.0	Formate	100	38	0
$ZnCl_2$	1.0	Alkyl silyl ether	100	32	0
$SnCl_2$	0.10	Alkyl silyl ether	50	42	50 [d]
$AlCl_3$	0.10	Alkyl silyl ether	55	60	45 [e]
$BF_3 \cdot Et_2O$	3.0	Borate ester	100	61	0
$ZnCl_2$	0.10	Alkyl silyl ether	100	67	0
trans-4-tert-butylcyclohexyl [c,f]	1.0	Symmetrical ether	100	63	
cis-4-*tert*-butylcyclohexyl [c,f]	1.0	Symmetrical ether	100	84	

[a] All reactions were run at room temperature. [b] Observed reduction product. [c] Data taken from ref. 22. [d] 27% *cis, cis-*, 53% *cis, trans-*, and 20% *trans, trans*-4-tert-butylcyclohexyl ether. [e] 43% *cis, cis-*, 45% *cis, trans-*, and 12% *trans, trans*-4-tert-butylcyclohexyl ether. [f] Reduction of $R_2C{=}\overset{+}{O}CHR_2$ (R_2CH = *cis-* or *trans*-4-tert-butylcyclohexyl, $R_2C{=}O$ = 4-tert-butylcyclohexanone) leading to symmetrical ethers during triethylsilane reduction of 4-tert-butylcyclohexanone in trifluoroacetic acid.

vate the carbonyl group in silane reductions dramatically affects the stereoselectivity of hydride transfer.

Because of competing symmetrical ether formation anhydrous aluminum chloride and stannous chloride were generally less satisfactory than either zinc chloride or boron trifluoride etherate for carbonyl group reductions by triethylsilane. In reductions catalyzed by zinc chloride, reaction stereoselectivity was remarkably sensitive to the amount of zinc chloride employed and to the reaction temperature. Reductions at room temperature, catalyzed by 10 mol% of zinc chloride with respect to 4-tert-butylcyclohexanone, led to 67% of the less stable alcohol derivative; in contrast, when equal amounts of zinc chloride and ketone were used reaction times were significantly shorter but the yield of *cis*-4-tert-butylcyclohexyl triethylsilyl ether was only 32%. Zinc chloride catalyzed triethylsilane reductions at 25° C were much slower than those run at 100° C but yielded a significantly higher relative yield of the less stable *cis*-isomer: 67% at 25° C, 33% at 100° C. These results are compatible with the coordination of zinc chloride with simple ketones to form mono- and di-carbonyl zinc chloride complexes (eq. 9, 10) [26.27]. Dicarbonyl complexes, offering greater steric restrictions for hydride transfer, promote reductions that yield predominantly the less stable alkyl silyl ether isomer. Similar coordination is not possible with boron trifluoride and, therefore, stereoselectivity in cyclic ketone reductions is not dependent on the molar ratio of ketone to boron trifluoride etherate.

$$R_2C{=}O + ZnCl_2 \rightleftharpoons R_2C{=}\overset{+}{O}{-}\overset{-}{Zn}Cl_2 \qquad (9)$$

$$R_2C{=}\overset{+}{O}{-}\overset{-}{Zn}Cl_2 + R_2C{=}O \rightleftharpoons (R_2C{=}O)_2ZnCl_2 \qquad (10)$$

Experimental

Methods and materials

Instrumentation has been previously described [22]. A Varian Model 485 digital integrator was used to determine peak areas in GLC analysis. Commercial boron trifluoride etherate was purified by distillation from calcium hydride through a 10 cm. Vigreux column under a slow flow of nitrogen and was stored over calcium hydride under nitrogen in a refrigerator at 5° C. Purified boron trifluoride etherate could be stored and used for more than six weeks without noticeable deterioration. Other anhydrous Lewis acids were commercial reagents and were not further purified. (+)-α-Naphthylphenylmethylsilane having an optical rotation of +31° (ether, 91% optical purity) and racemic α-naphthylphenylmethylmethoxysilane were prepared by the method of Sommer [11].

General reduction procedure in boron trifluoride etherate

Boron trifluoride etherate was added dropwise to an ice-bath cooled and rapidly stirred solution of the reduceable substrate and organosilane which were contained in a round bottom flask fitted with a condenser and drying tube. After addition was complete the homogeneous solution was allowed to warm to room temperature. In reactions with carbonyl compounds, addition of the boron trifluoride etherate initiated a mildly exothermic reaction. Generally a white precipitate formed as the reaction progressed. The progress of the reaction was followed by ^1H NMR analysis. Reaction times for aliphatic ketone and aldehyde reductions were less than one hour when one or more molar equivalents of $BF_3 \cdot Et_2O$ to carbonyl compound were used. Reductions of acetophenone and benzophenone were performed with a molar ratio of $BF_3 \cdot Et_2O$ to ketone between 1.0 and 2.5; these reactions were complete within two hours. Benzoic acid, benzamide, ethyl phenylacetate, nitrobenzene, and 1-methylcyclohexene were not reduced by triethylsilane even after reaction times as long as six days. Upon complete reduction, an excess of 3*N* sodium hydroxide was slowly added to the reaction mixture which was then stirred at room temperature for four hours. After approximately 5 min of hydrolysis the white solid had completely dissipated. The hydrolyzed mixture was then extracted three times with ether, the combined ether extract was dried over and filtered from anhydrous magnesium sulfate, and the magnesium sulfate filter cake was rinsed several times with small portions of ether. The combined ether washes and extract were concentrated under reduced pressure, and the products were subjected to ^1H NMR and GLC analyses. Triethylsilyl fluoride (>95%) and hexaethyldisiloxane (<5%) were the only silicon-containing products from reactions employing triethylsilane following hydrolysis, as determined by spectral and chromatographic analyses. Mass spectrum (70 eV) Et_3SiF: 136 (P + 2, 0.015), 135 (P + 1, 0.42), 134 (P, 3.20), 115 (45), 87 (12), 77 (100), 59 (30), 49 (29), 47 (33), 31 (10), 29 (11). Alcohols, symmetrical ethers, and alkenes were analyzed after hydrolysis; these compounds were the sole products from reductions of aliphatic ketones and aldehydes. Prior to hydrolysis borate ester products, $(RO)_nBF_{3-n}$, were inferred from ^1H NMR analyses: R = benzyl (s, δ 4.92 ppm), R = 1-octyl (t, δ 3.93 ppm), R = cyclohexyl (m, δ 4.35—3.85 ppm). These ^1H NMR spectra were identical to those of the tribenzyl, tri-1-octyl, and tricyclohexyl borate esters that were prepared from boric acid and the corresponding alcohols by standard procedures.

Synthesis of cyclohexene from cyclohexanone

Following complete reduction of cyclohexanone (5.0 g., 50 mmol) by triethylsilane (6.4 g., 55 mmol.) in $BF_3 \cdot Et_2O$ (3.08 g., 22 mmol.) the reaction mixture was directly distilled at atmospheric pressure. Two fractions were collected and analyzed by GLC and ^1H NMR spectroscopy: fraction 1, b.p. 35—83°C and fraction 2, b.p. 83—140°C. Fraction 2 was composed of 10.1 g. of a mixture of triethylsilane (0.6 g., 5.0 mmol), triethylfluorosilane (6.7 g., 50 mmol.), and cyclohexene (2.8 g., 34 mmol., 68% yield). Analysis of the pot residue after distillation showed cyclohexene, cyclohexyl ether, and unidentified materials.

Diphenylmethane from acylation-reduction

Boron trifluoride etherate (5.69 g., 40.2 mmol.) was added to a stirred solution of benzoyl chloride (1.43 g., 10.2 mmol), benzene (3.16 g., 40.5 mmol), and triethylsilane (3.58 g., 30.7 mmol) in a round bottom flask fitted with a reflux condenser and drying tube. After heating at 95°C for 18 h the reaction solution was cooled, quenched with 10% aqueous sodium hydroxide, and extracted as previously described. GLC analysis using an internal standard identified diphenylmethane in 30% yield. Identical yields of diphenylmethane were obtained when triethylsilane was added to the reaction solution subsequent to acylation of benzene by benzoyl chloride and when only 1.6 equivalent of $BF_3 \cdot Et_2O$, based on benzoyl chloride, was employed for acylation-reduction. Benzyl alcohol was not produced in these reactions. The relatively low yield of diphenylmethane was, therefore, a consequence of the acylation process rather than the reduction step and is consistent with yields from boron trifluoride etherate catalyzed acylation reactions that employ acid chlorides rather than acid fluorides [16].

Reactions with (+)-α-naphthylphenylmethylsilane

To a mixture of (+)-α-naphthylphenylmethylsilane (1.24 g., 5.0 mmol., 91% optical purity) and acetone (2.90 g., 50 mmol) in a round bottom flask was added 1.30 g. of $BF_3 \cdot Et_2O$ (9.2 mmol.). Extreme care was used to avoid the introduction of water into the reaction mixture: oven dried glassware was used, $BF_3 \cdot Et_2O$ was transferred by syringe, and reagents were added under a slow flow of nitrogen. After reduction was complete (2 h), as evidenced by the disappearance of the δ 5.39 (q, Si—H, $J = 4$ Hz) and 0.65 ppm (d, $Si—CH_3$, $J = 4$ Hz) signals and the appearance of the fluorosilane methyl doublet at δ 0.75 ppm ($J = 7.5$ Hz), the reaction solution was quenched with 15 ml. of saturated sodium bicarbonate. Pentane was added, the resulting mixture was extracted, and the aqueous solution was washed twice with pentane. The combined pentane solution was washed twice with water and was dried over anhydrous magnesium sulfate. Removal of pentane under reduced pressure gave an oil which was identified by ^1H NMR spectroscopy as the fluorosilane: (CCl_4, internal TMS) δ 0.75 (d, $J =$ 7.5 Hz, 3H) and 7.2—8.2 ppm (m, 13H). Distillation of the oil at 0.3 Torr gave α-naphthylphenylmethylfluorosilane (b.p. 129—132° C) in 78% isolated yield: $[\alpha]_D = -4.2°$ (ether, ca. 0.81). Recrystallization of the fluorosilane had no effect on the specific rotation. In an alternate workup procedure, employed for the majority of reductions with (+)-α-naphthylphenylmethylsilane, the reaction solution was evacuated to dryness after complete reduction. The remaining solid was was recrystallized twice from pentane to give the same stereochemical result. Net inversion (in parentheses) was observed for acetone reductions with relative silane: $BF_3 \cdot Et_2O$: acetone concentrations given: 1 : 1.80 : 10 (10%), 1 : 2.0 : 2.9 (13%), 1 : 1.9 : 2.3 (11%), 1 : 0.5 : 1.8 (9%). In a control experiment (+)-α-naphthylphenylmethylsilane was treated with a five-fold molar excess of BF_3-$\cdot Et_2O$. No change in the specific rotation of the silane was observed after three days at room temperature.

Reductions of menthone-isomenthone were performed as previously described. Racemic α-naphthylphenylmethylfluorosilane, isolated by a procedure identical to that used by Sommer [11a], was the only silicon product from these reactions. The olefinic proton from menthene was evident in ^1H NMR analyses of the reaction solutions (m, δ 5.2—5.3).

Attempted reductions of hexachloroacetone and di-tert-butyl ketone by (+)-α-naphthylphenylmethylsilane gave evidence for hydrolytic cleavage of naphthalene. In reactions with hexachloroacetone phenylmethylfluorosilane was formed and dissipated during a 16 day period at 50° C: ^1H NMR ($BF_3 \cdot Et_2O$, internal TMS) δ 0.40 (doublet of doublets, J ($F—CH_3$) = 7.5 Hz, J ($H—CH_3$) = 2.5 Hz, 3 H) and 5.22 ppm (doublet of quartets, J (F—H) = 54 Hz, J (CH_3—H) = 2.5 Hz, 1 H). Naphthalene was isolated and identified by spectral and GLC methods. Similar observations were made in reductions of di-tert-butyl ketone, but reaction times were three-times longer. No evidence for the reduction of these ketones by α-naphthylphenylmethylsilane was obtained. In a separate experiment naphthalene was formed from α-naphthylphenylmethylsilane and $BF_3 \cdot Et_2O$ when trace amounts of water were introduced into the reaction solution.

Reductions of alkyl-substituted cyclohexanones by triethylsilane in $BF_3 \cdot Et_2O$
Reactions were performed as previously described. Product yields were determined by GLC analyses. Isomeric alcohols from 2-, 3-, and 4-methylcyclohexanone reductions were separated and analyzed on 5 ft., 25% glycerol columns at 100°C. Isomeric alcohols from 4-tert-butylcyclohexanone reductions were separated and analyzed on a 5 ft. 20% Carbowax 20M column programmed from 135 to 180°C at 4°C/min. Isomeric alcohols from 3,3,5-trimethylcyclohexanone reductions were separated and analyzed on a 10 ft., 20% Carbowax 20M column at 180°C. The individual thermal conductivities of alcohol and symmetrical ether products were determined and used to obtain absolute yields. The thermal conductivities of the geometrical isomers of each alcohol were assumed to be identical [28]; those of the symmetrical ethers were identical within experimental error.

Triethylsilane reductions of 4-tert-butylcyclohexanone catalyzed by zinc chloride
Anhydrous zinc chloride was added to the solution of triethylsilane and 4-tert-butylcyclohexanone and the resulting mixture was stirred at 25°C or at 100°C. Reactions employing an equivalent amount of zinc chloride relative to ketone were complete within four hours at 25°C; however, as the reaction progressed a thick gel formed. Methylene chloride was used successfully to break up the gel to the point where good mixing of reagents occurred. Reactions employing 10 mol.% of zinc chloride relative to ketone were slow at room temperature; after two days less than 20% reduction had occurred. At 100°C reactions catalyzed by zinc chloride were complete within 24 h. Reaction solutions were quenched with excess saturated sodium bicarbonate and extracted with ether. The isomeric 4-tert-butylcyclohexyl triethylsilyl ethers were separated and anlyzed on a 5′ 15% SE-30 column at 200°C.

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References

1 M.P. Doyle, C.C. McOsker and C.T. West, J.Org. Chem., 41 (1976) 1393.
2 M.P. Doyle, D.J. DeBruyn, S.J. Donnelly, D.A. Kooistra, A.A. Odubela, C.T. West and S.M. Zonnebelt, J.Org. Chem., 39 (1974) 2740.
3 M.P. Doyle and C.T. West, J. Org. Chem., 40 (1975) 3835.
4 R. Calas, E. Frainnet and J. Bonastre, Compt. Rend., 251 (1960) 2987.
5 I.I. Lapkin, T.N. Povarnitsyna and L.A. Kostareva, Zh. Obshch. Khim., 38 (1968) 1578.
6 N.E. Glushkova and N.P. Kharitonova, Izvest. Akad. Nauk SSSR Ser. Khim., (1976) 88.
7 I. Ojima, J. Syn. Org. Chem. Jap., 32 (1974) 687.
8 K. Yamamoto, T. Hayashi and M. Kumada, J. Organometal. Chem., 54 (1973) C45.

9 W. Dumont, J. -C. Poulin, T. -P. Dang, and H.P. Kagan, J.Amer. Chem. Soc., 95 (1973) 8295.
10 R.J.P. Corriu and J.J.E. Moreau, J. Organometal. Chem., 64 (1974) C51.
11 (a) L.H. Sommer, C.L. Frye, G.A. Parker and K.W. Michael, J. Amer. Chem. Soc., 86 (1964) 3271; (b) L.H. Sommer, J.D. Citron and G.A. Parker, ibid., 91 (1969) 4729.
12 S.C. Pace, J.C. Elkaim and J.G. Reiss, J. Organometal. Chem., 56 (1973) 141.
13 E.J. Corey and A. Venkateswarlu, J. Amer. Chem. Soc., 94 (1972) 6190.
14 C.T. West, S.J. Donnelly, D.A. Kooistra and M.P. Doyle, J. Org. Chem., 38 (1973) 2675.
15 D.N. Kursanov, Z.N. Parnes and N.M. Loim, Synthesis, (1974) 633.
16 G.A. Olah, Friedel—Crafts and Related Reactions, Interscience Publishers, Inc., New York, N.Y., 1963—1964.
17 A.J. Vanderweilen and M.A. Ring, Inorg. Nucl. Chem. Lett., 8 (1972) 421.
18 L.H. Sommer, Stereochemistry, Mechanism and Silicon, McGraw-Hill, New York, N.Y., 1965, Chapter 4.
19 M.P. Doyle and C.T. West, J. Org. Chem., 40 (1975) 3829.
20 L.H. Sommer and D.L. Bauman, J. Amer. Chem. Soc., 91 (1969) 7076.
21 L.H. Sommer, W.D. Korte, and C.L. Frye, J. Amer. Chem. Soc., 94 (1972) 3463.
22 M.P. Doyle and C.T. West, J. Org. Chem., 40 (1975) 3821.
23 D.N. Kirk and A. Mudd, J. Chem. Soc., C, (1969) 804.
24 E.C. Ashby, J.R. Boone and J.P. Oliver, J. Amer. Chem. Soc., 95 (1973) 5427.
25 (a) H.C. Brown and S. Krishnamurthy, J. Amer. Chem. Soc., 94 (1972) 7159; (b) C.A. Brown, ibid., 95 (1973) 4100.
26 R.J. Berni, R.R. Benerito, W.M. Ayres and H.B. Jonassen, J. Inorg. and Nucl. Chem., 25 (1963) 807.
27 M. Nardelli, G. Fava and G. Giraldi, Acta Cryst., 16 (1963) 343.
28 E.L. Eliel, S.J. Schroeter, T.J. Brett, F.J. Biros and J.-C. Richer, J. Amer. Chem. Soc., 88 (1966) 3327.