Ionic and Organometallic-Catalyzed Organosilane Reductions

GERALD L. LARSON and JAMES L. FRY

WILEY

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IONIC AND ORGANOMETALLIC-CATALYZED ORGANOSILANE REDUCTIONS . . . .
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FOREWORD

Chemical synthesis is an intellectually and technically challenging enterprise. Over the many decades of progress in this discipline, spectacular advances in methods have made once intimidating transformations now routine. However, as the frontier advances and the demands for ready access to greater molecular complexity increases, so does the sophistication of the chemical reactions needed to achieve these goals. With this greater sophistication (and the attendant expectation of enhanced generality, efficiency, and selectivity) comes the challenge of adapting these technologies to the specific applications needed by the practitioner. In its 67-year history, *Organic Reactions* has endeavored to meet this challenge by providing focused, scholarly, and comprehensive overviews of a given transformation.

By any yardstick, the reduction of organic compounds is one of the most important methods for the manipulation of functional groups. No fewer than 27 of the 245 chapters in the *Organic Reactions* series are dedicated to reduction in one if its manifold forms. Among the mildest of these transformations is the use of ubiquitous organosilanes. Because of the wide range of organosilanes available and the different mechanisms by which they can be activated to transfer the hydride, these reagents have found extensive application in organic synthesis. A startling array of different functional groups can be reduced by organosilanes with high selectivity. The oxidized organosilane byproducts are easily removed and non-toxic. Moreover, some of the most exciting recent developments involve the enantioselective reduction of double-bonded functional groups.

The *Organic Reactions* series is fortunate to have published a timely chapter on this important process that single-handedly constituted Volume 71. This comprehensive chapter was authored by two of the internationally recognized leaders in this field, Dr. Gerald L. Larson and Prof. James L. Fry. Although many reviews and book chapters have been written on reductions with organosilanes, this massive work constitutes the definitive treatise in the field. Thus, in keeping with our educational mission, the Board of Editors of *Organic Reactions* has decided to publish this chapter as a separate, soft cover book to make the work available to a wider audience of chemists. In addition, to keep pace with the rapid development of this field, Drs. Larson and Fry have provided updated references that bring the literature coverage up to March 2009. These references are appended at the end of the original reference section and organized by the Tabular presentation of the different substrates for reduction.

The publication of this book represents the third soft cover reproduction of single-volume *Organic Reactions* chapters. The success of the first two soft cover books ("The Stille Reaction" taken from Volume 50 and "Handbook of Nucleoside Synthesis" taken from Volume 55) has convinced us that the availability of low-cost, high-quality publications that cover broadly useful transformations is addressing an unmet need in the organic synthesis community. Thus we will continue to identify candidates for the compilation of such individual volumes as opportunities present themselves.

Scott E. Denmark
Urbana, Illinois

PREFACE

The reduction of organic functional groups ranks as one of the most important transformations in synthetic organic chemistry. The range of reagents for organic reductions spans from the highly-reactive, highly-nucleophilic metal hydrides at one extreme, to the inert dihydrogen molecule at the other. In view of the variety of organic functional groups that are subject to reduction, highly selective reducing agents are needed. Organosilanes are particularly well suited to meet this challenge because they can be electronically and sterically modified to finely tune their reactivity and thus achieve a number of chemoselective reductions. The substrates in ionic organosilane reductions require activation by an acid or organometallic catalyst. Thus, the reaction selectivity can be further optimized by the choice of activator. Organosilane reduction of essentially all reducible organic functional groups including aromatic rings, aryl halides, carboxylic acids, and amides have been achieved. Moreover, the use of chiral ligands and chiral organometallic catalysts in conjunction with organosilanes has allowed the enantioselective reduction of ketones, imines, enamines, enones, enals, and α,β-unsaturated esters with extremely high selectivities.

Experimental reaction conditions are discussed and numerous specific experimental procedures are provided from the literature for a wide spectrum of representative functional group transformations using this method. A tabular survey of all examples of organosilicon hydrides used in organic synthesis is presented in 34 tables organized by type of substrate reduced with listings within each table according to increasing carbon number of the substrates.

The literature is covered through March 2009, supplementing the coverage used in the earlier hard cover chapter. These latest literature references have been collected in separate sections according to the sequence of the tables in the tabular survey section. In each of the sections, the individual citations have been arranged in alphabetic order of the author names.

Ionic and Organometallic-Catalyzed Organosilane Reductions is intended to be a useful, easily read tool for all practitioners of organic synthesis.

IONIC AND ORGANOMETALLIC-CATALYZED ORGANOSILANE REDUCTIONS

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INTRODUCTION

The purpose of this chapter is to present a critical review of synthetically useful variations of ionic methods for hydrogenation of organic compounds. In practice, ionic hydrogenation involves the formal introduction of hydride from a donor source to an electron-deficient carbon center. The electrophilic centers can be formed by the departure of a leaving group (nucleofuge) from a saturated center or by the addition of an electrophile to a multiple bond. In the former mechanism, substitution of hydrogen for the leaving group is the net chemical consequence. In the latter, addition across the multiple bond is the result.

In this chapter, we cover the use of organosilicon hydrides as the source of ionic hydride with the goal of completing and updating earlier review works on the subject.[1-4] Similar chemistry is observed when molecular hydrogen[5,6] or various hydrocarbons[7-9] are used as hydride sources; these methods have been reviewed previously and are not covered herein. The use of organosilicon hydride-metal catalyst mixtures[10-12] for effecting reductions is included in this review, but use of trichlorosilane-tertiary amine combinations[13] is not.

Organosilicon compounds with at least one Si-H bond (called hydrosilanes, organosilicon hydrides, or simply silanes) have the ability to serve as mild air- and water-stable sources of hydride and thus have reducing properties. For example, triethylsilane is reported to reduce a variety of inorganic metal salts directly to the free metals.[14,15] Even the hexachloroantimonate anion can be reduced to Sb(0) upon contact with this silane.[16] Organotellurium chlorides are reduced to tellurium metal by a number of organosilicon hydrides.[17] Reaction of organosilicon hydrides with strong Brønsted acids leads to decomposition of the silane and the production of hydrogen gas.[14] In general, organosilicon hydrides do not undergo spontaneous reactions with organic compounds unless the organic substrate is a reasonably strong electrophile or the silane has been first activated by the interaction of a nucleophilic species with the silicon center. The organosilicon hydrides are covalent compounds that have little or no nucleophilic properties of their own. Aside from the parent silane, SiH_4, which is pyrophoric, the organosilicon hydrides are fairly innocuous compounds whose physical properties bear resemblance to their hydrocarbon analogs. Thus, their physical and chemical reducing properties differ from those of many familiar metal hydride reducing agents.[18,19] The use of organosilicon hydrides often provides a means of effecting reductions of organic substrates under very mild conditions and with excellent functional group selectivity.

Consideration of the nature of the Si–H bond provides insight into the chemical behavior of organosilicon hydrides. Comparison of the bond strengths as represented by bond dissociation energy (BDE) of hydrosilanes with those of hydrocarbon analogs shows that, in general, the Si–H bond is not much weaker than the C–H bond. Thus, the BDE values for the respective Si–H bonds in TMS–H and $(C_2H_5)_3Si–H$ are 90.3[20] and 90.1 kcal/mol[21] compared with a value of approximately 92 kcal/mol[20] for the tertiary C–H bond in $(CH_3)_3C–H$. On the other hand, there is a significant difference between the polarization characteristics of the Si–H and C–H bonds.[22] Compared to the Pauling electronegativity of hydrogen (2.20), the electronegativity of carbon (2.50) is greater and that of silicon (1.90) is less.[23] Carbon-hydrogen bonds are thus polarized in the direction $C^{\delta-}–H^{\delta+}$, whereas Si–H bonds are $Si^{\delta+}–H^{\delta-}$. As will be seen, this enhanced hydridic nature manifests itself in the chemical behavior of essentially all hydrosilanes.

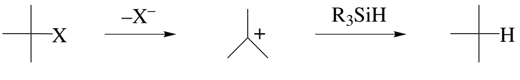
Limited studies of the germanium and tin hydride analogs of the silicon hydrides show that they share this ability to function as hydride sources in ionic hydrogenations; however, their relatively greater reactivity toward acids appears to restrict their practical applications in organic synthesis.[24,25]

MECHANISM

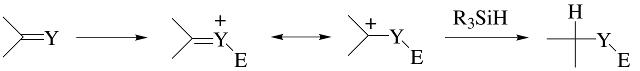
General Considerations

The mechanistic discussion of silane reductions will be limited to those of cationic reductions, thus excluding the many silane reductions that involve metal catalysis.

Since tetravalent organosilicon hydrides intrinsically lack nucleophilicity, they react only with atomic centers that are substantially electron deficient, for example, carbocations. Because of this, organosilicon hydride reductions are potentially very selective. The "ionic" reductions of organic compounds by organosilicon hydrides are understood on the basis of two mechanisms. In the first, substitution by hydrogen of a leaving group bonded to a saturated carbon occurs. This path may be called a σ-route as it involves the stepwise cleavage of a σ-bond to a saturated center and the intervention of a carbocation intermediate that is captured by donation of hydride from the organosilicon hydride (Eq. 1). Alternatively, addition of an electrophile/hydride pair takes place across a multiple bond. This path may be termed a π-route (Eq. 2). Complexation of an electrophile to one end of a π-bond is followed by capture of the intermediate cation or complex by organosilicon hydride. The electrophile may be as simple as a proton or be one of a variety of Lewis acids or alkylating agents. The group Y can be C, O, N, or S. Sometimes the product of Eq. 2 can continue reacting by way of Eq. 1, with the moiety Y–E acting as a leaving group. When this occurs, the net effect is to replace the C=Y functionality with CH_2. The normal caveats regarding carbocation behavior such as the possible occurrences of eliminations, skeletal isomerizations, and bimolecular reactions prior to capture by hydride must be expected in all of these scenarios.

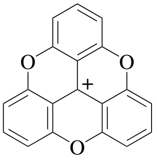


(Eq. 1)



(Eq. 2)

It is necessary for the intermediate cation or complex to bear considerable carbocationic character at the carbon center in order for effective hydride transfer to be possible. By carbocationic character it is meant that there must be a substantial deficiency of electron density at carbon or reduction will not occur. For example, the sesquixanthydryl cation **1**,[26] dioxolenium ion **2**,[27] boron-complexed imines **3**, and O-alkylated amide **4**,[28] are apparently all too stable to receive hydride from organosilicon hydrides and are reportedly not reduced (although the behavior of **1** is in dispute[29]). This lack of reactivity by very stable cations toward organosilicon hydrides can enhance selectivity in ionic reductions.



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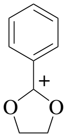

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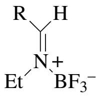

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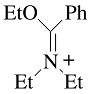


4

Role of Trivalent Silicon Species

The overall stoichiometry of hydride transfer from a silicon center to an electron-deficient carbon center is quite straightforward. Almost without exception, it appears that there is simple interchange of hydride to the carbocation while the silicon center receives the elements of the carbocation's counterion (Eq. 3).

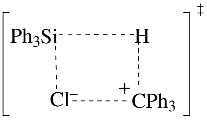
$$R_3C^+X^- + R'_3SiH \longrightarrow R_3CH + R'_3SiX \qquad \text{(Eq. 3)}$$

When the counterion is complex, for example metal-halogen anions such as BF_4^-, the most electronegative portion of the counterion becomes attached to the silicon center. Because of this attachment, it is natural to consider the intermediacy of a silicenium cation (silylium or silylenium ion) intermediate in such reactions (Eq. 4). Bond energies derived from electron impact studies indicate that Eq. 4 is exothermic in the gas phase by about 8 kcal/mol.[26,29] There seems little doubt that trivalent silicon-centered cationic species do exist in the gas phase[30,31] or that processes similar to that shown in Eq. 4 do occur there.[32,33]

$$Me_3C^+ + (CH_3)_3SiH \longrightarrow (CH_3)_3CH + (CH_3)_3Si^+ \qquad \text{(Eq. 4)}$$

The existence of trivalent silicenium cations as reactive species in solution is more controversial. Many early attempts to demonstrate the solution-phase existence of stable silicenium ions by using techniques analogous to those successfully applied to carbocation formation failed.[34–36] Other reports of attempts to generate silicenium ions in solution under stable ion conditions[37–46] and in solvolyses[47] are more convincing, but not without controversy.[48–51] The single-crystal X-ray determination of a non-planar triethylsilylium moiety paired in the crystalline state with the tetrakis(pentafluorophenyl)borate gegenion and toluene solvate stirred much debate about its interpretation and extension to reaction systems.[52,53] Recent crystallographic evidence supports the notion of a three-coordinate structure of a trimesitylsilylium cation paired with a carborane anion in the solid phase.[54,55] The balance of experimental evidence seems to indicate that, whereas trivalent silicenium cations may have fleeting existence as reaction intermediates, it is unlikely that they exist as stable, long-lived species in solution.[56] The failure to observe such trivalent species in solution is related to the very strong ability of electron-deficient silicon centers to coordinate with the media in which they are formed.[53,57,58] This is true even in solvents that exhibit little or no nucleophilicity toward carbocations and is further enhanced by the relatively long bond lengths to silicon centers that allow a close approach by coordinating species.[53]

The available experimental information is suggestive, but not unambiguously conclusive, of the intervention of electron-deficient silicon-centered species that may resemble silicenium cations in simple hydride exchanges occurring in solvents with low coordinating abilities. For example, substituted triarylmethane derivatives such as chlorotriphenylmethane (trityl chloride) undergo reduction through halogen-hydride exchange with organosilicon hydrides. The reactions proceed more rapidly in solvents with high ionizing power, but are kinetically first order with respect to both organosilicon hydride and triarylmethane derivative in benzene solvent.[59] In benzene, the exchange of halogen with hydride occurs with retention of configuration at the silicon center.[60] These results have led to the suggestion that the exchanges proceed by way of a four-center transition state **5**, in which there is simultaneous attack by the halide of the carbocation-halide ion pair on the silicon center as hydride undergoes transfer to the carbocation center.[60]



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Simple variation of the solvent has a very significant effect on the stereochemistry at the silicon center for these exchange reactions. The stereochemistry changes from essentially complete retention to inversion and even to racemization. For example, in dichloromethane the halogen is delivered to the silicon center with complete racemization.[61] This implies that the degree of "tightness" of the carbocation-counterion pair must change depending on the solvent.

Organosilicon hydride reductions of preformed stable carbocations such as triphenylmethyl (trityl) tetrafluoroborate and hexafluoroantimonate salts are rapid and essentially quantitative.[62,63] Reductions of these and similar stable ions in dichloromethane/trifluoroacetic acid (TFA) show primary deuterium kinetic isotope effects in the range $k_H/k_D = 1.27$[64] to 1.89[65] at room temperature, whereas effects equal to $k_H/k_D = 1.50–2.33$ are seen for the reduction of diarylcarbenium ions with deuteriosilanes at −70°.[66] The kinetic rate dependence for similar reactions in acetic acid is first order in both the cation and the silane. The rates of a series of substituted arylsilanes correlate with σ constants, but not with σ^+ constants, to produce Hammett plots with $\rho = -1.84$ for triarylsilanes and $\rho = -1.01$[65] to −2.46[66] for aryldimethylsilanes. These results are interpreted to mean that the reactions occur through a four-center transition state in which the silicon center assumes a trigonal-bipyramidal shape with hydride exiting from an equatorial position while the carbocation's counterion approaches axially.[65]

Trityl and tropylium (cycloheptatrienyl) cation salts having complex metal-halide anions such as SbX_6^-, AsF_6^-, PF_6^-, $FeCl_4^-$, and BF_4^- undergo reduction with trialkylsilanes and aryldialkylsilanes at rates that are independent of the nature of the anion or of ring strain in the organosilicon hydride, are kinetically first order with respect to both cation and organosilicon hydride, and that display primary deuterium kinetic isotope effects of $k_H/k_D = 1.41–1.49$ in dichloromethane.[67,68] It is argued that these reactions proceed by way of a three-step mechanism involving a rate-determining single-electron transfer step[69] to create a charge-transfer complex between the carbocation and the organosilicon hydride followed by a faster transfer of hydride to the carbon center and the creation of a silicenium ion intermediate that is then rapidly captured by the counterion present (Eq. 5).[68] Others regard this argument as doubtful compared to the polar mechanism in which Si–H bond cleavage is rate determining.[66]

$$\begin{aligned} &R'_3SiH + R_3\overset{+}{C} \rightleftharpoons \left[R'_3SiH\text{---}\overset{+}{C}R_3\right] \xrightarrow{\text{slow}} \\ &R'_3\overset{+}{Si}\text{----}H{-}CR_3 \longrightarrow R'_3\overset{+}{Si} + R_3CH \end{aligned} \qquad \text{(Eq. 5)}$$

Uncertainties in understanding the exact mechanistic details of these reactions are sure to stimulate continued work to define the nature of trivalent silicon cations in ionic reductions by organosilicon hydrides.

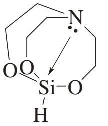
Role of Hypervalent Silicon Species

It is well known that strong electrophiles such as carbocations are reduced by organosilicon hydrides (Eq. 1).[3,70,71] On the other hand, simple mixtures of organosilicon hydrides and compounds with weakly electrophilic carbon centers such as ketones and aldehydes are normally unreactive unless the electrophilicity of the carbon center is enhanced by complexation of the carbonyl oxygen with Brønsted acids[3,70–73] or certain Lewis acids (Eq. 2).[1,70,71,74,75] Using these acids, hydride transfer from the silicon center to carbon may then occur to give either alcohol-related or hydrocarbon products.

Alternatively, unreactive mixtures of organosilicon hydrides and carbonyl compounds react by hydride transfer from the silicon center to the carbon center when certain nucleophilic species with a high affinity for silicon are added to the mixture.[76–94] This outcome likely results from the formation of valence-expanded, pentacoordinate hydrosilanide anion reaction intermediates that have stronger hydride-donating capabilities than their tetravalent precursors (Eq. 6).[22,95–101]

$$R_3SiH + Nu^- \rightleftharpoons R_3SiHNu^- \xrightarrow[2.\ H_2O]{1.\ R'_2C{=}O} R_3SiNu + R'_2CHOH \qquad \text{(Eq. 6)}$$

The bicyclic silatrane molecule **6**, which has a strong degree of coordination between the silicon center and the nitrogen bridgehead, has been shown to have unusually strong reducing properties compared to normal tetravalent organosilicon hydrides.[102] The hypothesis that valence-expanded pentacoordinate silicon species are the actual reducing species[76,77,83] is plausible, for such species are well known.[96,99,101,103–107] Other examples are known of the enhanced reducing powers of organosilicon hydrides that undergo intramolecular coordination and expansion to pentavalent[82] and even hexavalent states.[84,101,108–111]



6

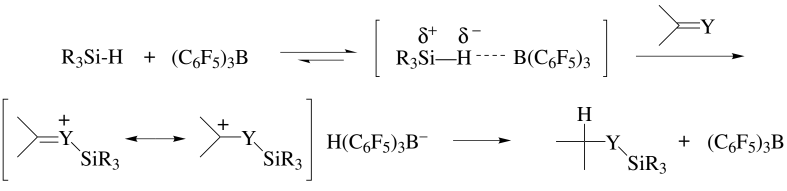
A variety of nucleophilic species cause valence expansion of organosilanes and the enhancement of reducing reactivity. These include formate, thiocyanate, tartrate, and phthalate salts,[78] as well as alkoxides[91,92,96,99,107] and catecholates.[93] The strong propensity of fluoride ion to cause silicon centers to undergo valence expansion[95,112] makes it especially effective in activating organosilicon hydrides as reducing agents. Aldehydes, ketones, and esters may all be reduced by such a technique, frequently with excellent functional group and stereochemical selectivity.[76–89]

The valence-expanded silicon intermediate retains some measure of stereochemical integrity up to the point of hydride transfer as evidenced by the small degrees of asymmetric induction that are observed in the reduction of prochiral ketones coupled with similar degrees of chirality found at the silicon center.[85] The transfer of hydride from the silicon center to the carbonyl carbon takes place in the rate-determining step as judged by the primary deuterium kinetic isotope effect of 1.50 observed in the fluoride-induced reduction of acetophenone with dimethylphenylsilane-d_1.[88] There is also evidence that the pentacoordinate silicon hydride can serve as a single-electron-transfer donor since radical-coupling products are sometimes obtained, although the general importance of this process is open to question.[89,99]

A diaryldihydrosilane with a hexacoordinated silicon center, produced through intramolecular coordination, is reported not to react with benzaldehyde, although the silane is capable of reducing silver ion to silver metal.[113] There is also a report of a heptacoordinate silicon hydride species with the ability to transfer hydride to trityl cation while remaining inactive toward methanol.[108,114]

Role of O/N-Silylated Cationic Intermediates

An interesting variation of the reaction mechanisms discussed above has been offered following studies of the hydrosilation reductions of aldehydes, ketones, and esters to their corresponding silyl ethers and acetals, respectively, when catalyzed by tris(pentafluorophenyl)borane, $(C_6F_5)_3B$,[115,116] and related boranes.[117] This mechanism proposes a pathway in which the first step is the reversible formation of a linear silane-borane adduct that undergoes subsequent nucleophilic attack by the carbonyl compound of the substrate to yield an O-silylated cationic intermediate along with a boron hydride anion.[118] The boron hydride ion then transfers a hydride to the carbon center of the O-silylated cation to yield the reduction product and regenerated free borane. A simplified view of the suggested mechanism is shown below (Scheme 1). Similar reaction paths have been proposed for the hydrosilation of enones and silyl ethers[119] as well as imines.[120]



Scheme 1

Role of Metal Catalysts

A wide variety of metals can effectively catalyze the reduction of multiple bonds by organosilicon hydrides (Eq. 2). No doubt, the function of some of these metals is to serve as Lewis acids by adding to the most electron-rich end of a bond and promoting transfer of hydride to the other center. On the other hand, it is clear that many transition metal complexes function through significantly different and more complex catalytic pathways to promote silane reductions. A common reaction stage suggested for many of the catalytic cycles is the creation of a reactive intermediate having a metal-hydrogen bond that is formed by hydrogen transfer from the silane to the catalytic metal center.[116] This reducing center, often with appropriate coordinating ligands, subsequently delivers hydrogen to the substrate and the metal center is freed for additional catalytic cycles. When the catalytic metal ligands are chiral, this process can lead to very high degrees of enantiomeric selectivity in the reduction of prochiral substrates.[121–125]

SCOPE AND LIMITATIONS

Reduction of Substituted Alkanes

Alcohols to Alkanes. Many alcohols are converted directly into hydrocarbons when treated with acid in the presence of organosilicon hydrides (Eq. 7). The mechanism normally follows the pathway shown in Eq. 1.

$$\mathrm{ROH} \xrightarrow[\mathrm{R'_3SiH}]{\text{"acid"}} \mathrm{RH} \qquad \text{(Eq. 7)}$$

The reaction generally proceeds cleanly and in high yields (70–100%) when the starting alcohol permits the formation of reasonably stable carbocation intermediates. Alcohols capable of producing carbenium ions spanning a range of stabilities of more than 24 pK_{R+} units undergo this reduction.[26] Depending on the reaction conditions, secondary[126] and tertiary[127] aliphatic alcohols, secondary and tertiary benzylic alcohols,[26,126] some ring-substituted primary benzylic alcohols,[26,128,129] and cyclopropylcarbinols[130] are reduced to the corresponding alkanes. However, olefinic and rearrangement products can occur from side reactions under these acid conditions.[126,131,132] Phenols are not reduced under the same conditions.

Almost any organosilicon hydride causes reduction of the cations produced, although the order of reactivity of simple alkyl and aryl-substituted silanes is observed to be triethyl > trioctyl ∼ diethyl > diphenyl ∼ triphenyl.[26] A detailed quantitative study of the reactions of organosilicon hydrides with diarylcarbenium ions in dichloromethane at −70° indicates a relative reactivity order of $R_3SiH > R_2SiH_2 > RSiH_3$, with alkyl substituent groups generally producing greater reactivity than aryl substituents.[61] Use of a deuterated silane yields the corresponding deuterated hydrocarbon (Eq. 8).[127,133,66]

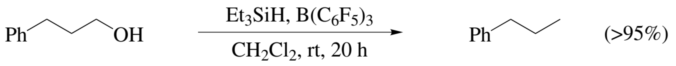
$$\mathrm{ROH} \xrightarrow[\mathrm{R'_3SiD}]{\text{"acid"}} \mathrm{RD} \qquad \text{(Eq. 8)}$$

Normally, only a small stoichiometric excess (2–30 mol%) of silane is necessary to obtain good preparative yields of hydrocarbon products. However, because the capture of carbocation intermediates by silanes is a bimolecular occurrence, in cases where the intermediate may rearrange or undergo other unwanted side reactions such as cationic polymerization, it is sometimes necessary to use a large excess of silane in order to force the reduction to be competitive with alternative reaction pathways. An extreme case that illustrates this is the need for eight equivalents of triethylsilane in the reduction of benzyl alcohol to produce only a 40% yield of toluene; the mass of the remainder of the starting alcohol is found to be consumed in the formation of oligomers by bimolecular Friedel-Crafts-type side reactions that compete with the capture of the carbocations by the silane.[129]

Both Brønsted and Lewis acids are effective in coordinating with the hydroxyl oxygen to induce heterolysis of the C–O bond and cause formation of the necessary carbocation intermediate. The reactions are frequently conducted under homogeneous conditions in inert solvents such as dichloromethane or chloroform. Conditions used include the treatment of alcohols with organosilicon hydrides in neat acetic acid,[26,29] neat trifluoroacetic acid[134] or trifluoroacetic acid/ammonium fluoride[135] as well as mixtures of trifluoroacetic acid,[26] methanesulfonic acid,[126] or triflic (trifluoromethanesulfonic) acid with triflic anhydride[126] in dichloromethane or chloroform, mixtures of acetic acid and sulfuric or *p*-toluenesulfonic acid,[134] acetic acid and hydrogen chloride/aluminum chloride,[136] and boron trifluoride[126] or boron trifluoride etherate in dichloromethane[137,133] or chloroform.[138] The use of very strong Brønsted acids such as methanesulfonic and triflic acids may cause decomposition of the organosilane through hydrogen production[14] and/or cleavage of Si–C bonds[139] which compete with the desired reduction of the alcohol.[126] These undesirable side reactions may be avoided or reduced by running the reaction at −78°.[140] Sulfuric acid may cause undesirable oxidations to occur.[134] On balance, the most commonly chosen set of conditions for the reduction of alcohols is triethylsilane and trifluoroacetic acid (Et_3SiH/TFA) in dichloromethane solution.

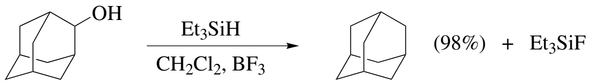
The experimental evidence is convincing, at least with benzyl alcohols, that a "free" carbenium ion intermediate devoid of influence from its progenitor is the species that is captured by the non-nucleophilic organosilicon hydride. When optically active 2-phenyl-2-butanol is treated with Et_3SiH/TFA in chloroform, the 2-phenylbutane product is formed with complete racemization.[26] When a dichloromethane solution of the same alcohol is treated with trifluoroacetic acid in the presence of enantiomerically enriched 1-naphthylphenylmethylsilane, the 2-phenylbutane product obtained shows a small, but reproducible enantiomeric excess of 2–3%.[141] The predominant enantiomer formed in the product is dependent only on the predominant enantiomer of silane used as the reducing agent and is independent of whether one of the pure enantiomers or the racemic alcohol is used as substrate.[142] The same stereochemical results are obtained in the hydrocarbon product when the alkene 2-phenyl-1-butene is the precursor to the carbenium ion intermediate (π-route, Eq. 2) instead of the tetrahedral alcohol (σ-route, Eq. 1).[142] A similar conclusion is reached from a study of the reduction of optically active 1-phenylethanol to phenylethane-d_1 with boron trifluoride etherate and triethylsilane-d_1.[133] These experiments illustrate the lack of nucleophilicity or S_N2-like behavior of the organosilicon hydrides in these reactions and presage the stereochemistry expected from such transformations.

Primary Alkyl Alcohols. Primary alkyl alcohols do not undergo reduction when treated with Brønsted acids and organosilicon hydrides under usual laboratory conditions.[143] This reflects the relative instability of primary alkyl carbenium ions in the condensed phase and the weak intrinsic nucleophilicity of organosilicon hydrides. On the other hand, the combination of excess Et_3SiH and catalytic amounts (5–10 mol%) of $(C_6F_5)_3B$ reduces primary aliphatic alcohols to the alkanes in high yields (Eq. 9), but the reaction stops at the non-reductive silylation of the alcohol with only a single equivalent of the silane.[144,145] This type of reaction is thought to proceed via a direct nucleophilic displacement rather than by way of a carbenium ion mechanism.[145]



(Eq. 9)

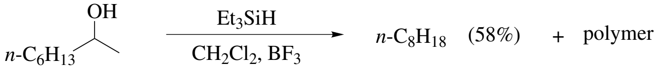
Secondary Alkyl Alcohols. Treatment of secondary alkyl alcohols with trifluoroacetic acid and organosilicon hydrides results only in the formation of the trifluoroacetate esters; no reduction is reported to occur.[1,2] Reduction of secondary alkyl alcohols does take place when very strong Lewis acids such as boron trifluoride[126,129] or aluminum chloride[136,146] are used. For example, treatment of a dichloromethane solution of 2-adamantanol and triethylsilane (1.3 equivalents) with boron trifluoride gas at room temperature for 15 minutes gives upon workup a 98% yield of the hydrocarbon adamantane along with fluorotriethylsilane (Eq. 10).[129]



(Eq. 10)

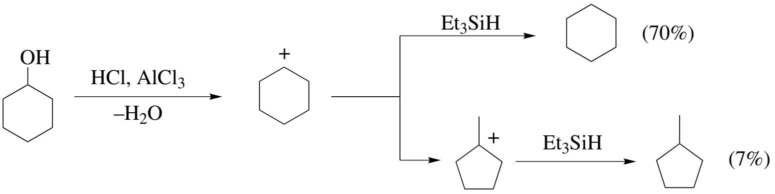
In contrast, when boron trifluoride etherate is substituted for the free boron trifluoride, only a trace of the hydrocarbon is formed, even after weeks of reaction.[143] The unique effectiveness of boron trifluoride gas in promoting these reductions is believed to be due to several factors, including the ability of the coordinatively unsaturated boron center to rapidly and tightly coordinate with oxygen centers and to the thermodynamically favorable creation of a Si–F bond.[1] A slight pressure of boron trifluoride gas must be maintained over the surface of the solution throughout the reaction because boron trifluoride has only limited solubility in the weakly coordinating dichloromethane solvent.

The formation of alkenes and alkene-related polymerization products can seriously reduce the yields of desired alkane products from secondary alcohols, which can undergo elimination reactions. For example, reduction of 2-octanol at 0° with boron trifluoride gas in dichloromethane containing 1.2 equivalents of triethylsilane gives only a 58% yield of *n*-octane after 75 minutes (Eq. 11).[129] The remainder of the hydrocarbon mass comprises nonvolatile polymeric material.[126]



(Eq. 11)

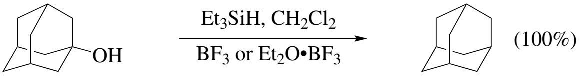
Aluminum chloride, used either as a stoichiometric reagent or as a catalyst with gaseous hydrogen chloride, may be used to promote silane reductions of secondary alkyl alcohols that otherwise resist reduction by the action of weaker acids.[136] For example, cyclohexanol is not reduced by organosilicon hydrides in the presence of trifluoroacetic acid in dichloromethane, presumably because of the relative instability and difficult formation of the secondary cyclohexyl carbocation. By contrast, treatment of cyclohexanol with an excess of hydrogen chloride gas in the presence of a three-to-four-fold excess of triethylsilane and 1.5 equivalents of aluminum chloride in anhydrous dichloromethane produces 70% of cyclohexane and 7% of methylcyclopentane after a reaction time of 3.5 hours at room temperature (Eq. 12).[136] The cyclohexane is presumably formed by capture of the secondary cyclohexyl cation, whereas the methylcyclopentane must arise from hydride capture of the more stable tertiary methylcyclopentyl cation formed by rearrangement of the cyclohexyl cation.[147,148] Diminishing the amount of aluminum chloride to only 0.5 equivalents results in no reaction after one-half hour and the formation of only 8% of cyclohexane after four hours reaction time. The reaction proceeds slowly in the absence of hydrogen chloride, producing 53% of cyclohexane and 6% of methylcyclopentane after 16.5 hours using two equivalents of aluminum chloride.



(Eq. 12)

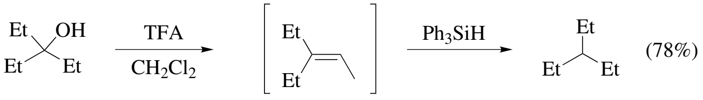
Tertiary Alkyl Alcohols. Tertiary alkyl alcohols generally undergo facile reduction when treated with acids in the presence of organosilicon hydrides.[127,136] This comparative ease of reduction reflects the enhanced stability and ease of formation of tertiary alkyl carbenium ions compared with primary and secondary carbenium ions. Thus, treatment of 1-methylcyclohexanol with mixtures of triethylsilane and aluminum chloride in dichloromethane produces near quantitative yields of methylcyclohexane with or without added hydrogen chloride in as little as 30 minutes at room temperature, in contrast to the more vigorous conditions needed for the reduction of the secondary alcohol cyclohexanol.[136]

Similarly, and in contrast to the behavior of its secondary isomer, 2-adamantanol, 1-adamantanol undergoes smooth, quantitative reduction to adamantane in less than an hour at room temperature in dichloromethane solution containing triethylsilane under the catalysis of either free boron trifluoride[129] or boron trifluoride etherate (Eq. 13).[143]



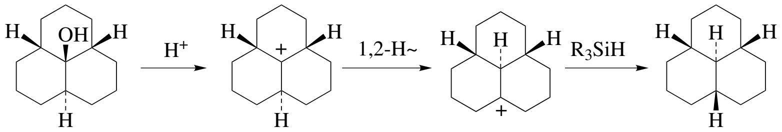
(Eq. 13)

Although the synthetic yields of hydrocarbon products obtained from the reduction of tertiary alkyl alcohols are frequently quite high, studies show that the reaction pathways taken by the reactants are not always as direct or straightforward as might be suggested by the structural relationships between reactants and products. For example, preparative-scale treatment of a dichloromethane solution of 3-ethylpentan-3-ol and triphenylsilane (1.2 equivalents) with excess trifluoroacetic acid (1.5 M) at room temperature for 24 hours gives 3-ethylpentane in 78% yield (Eq. 14).[127] Under these reaction conditions, the alcohol rapidly undergoes elimination to 3-ethyl-2-pentene, which is the actual species undergoing reduction.



(Eq. 14)

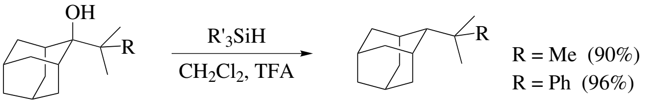
The tertiary alcohol *cis,cis,trans*-perhydro-9*b*-phenalenol (**7**) is converted stereospecifically and in high yield (92%) to *trans,trans,trans*-perhydrophenalene (**10**) when treated with either triethylsilane or triphenylsilane and trifluoroacetic acid in dichloromethane (Eq. 15). Studies indicate that the reaction path follows the cation rearrangement **8** → **9** and that the trans trifluoroacetate ester related to cation **9** is an intermediate, which accumulates during the reaction.[127]



7 **8** **9** **10** (92%)

(Eq. 15)

The conversion of alcohols directly into the structurally related hydrocarbons by ionic hydrogenation can provide a means of synthesis for compounds that would be extremely difficult or impossible to obtain by other methods. A good example is the synthesis of 2-*tert*-butyladamantane (**12**, R = Me). This interesting, highly strained compound may be synthesized in moderate overall yield by a conventional multiple-step route.[149] Alternatively, it is obtained in 90% isolated yield upon treatment of a dichloromethane solution of the readily available 2-*tert*-butyl-2-adamantanol (**11**, R = Me)[150] and one equivalent of either tri-*n*-hexylsilane[151,152] or triethylsilane[153] with trifluoroacetic acid at room temperature (Eq. 16).

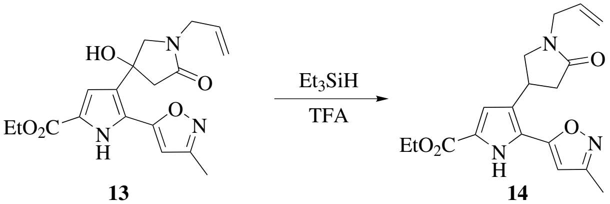


11 **12**

(Eq. 16)

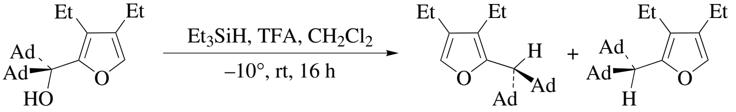
In a similar fashion, 2-cumyladamantane (**12**, R = Ph) is formed in nearly quantitative yield upon treatment of the easily synthesized 2-cumyl-2-adamantanol (**11**, R = Ph)[154] with triethylsilane and methanesulfonic acid in dichloromethane at −78°.[155] The high yield of a single very strained hydrocarbon product in each reaction is quite surprising in view of the very complex interconversions of carbocations known to take place from the alcohol precursors.[140,151,152,156]

The remarkable chemoselectivity of this reductive technique is demonstrated by the conversion of the functionally rich compound **13** into **14** in 86% yield upon treatment with Et_3SiH/TFA at room temperature for two hours (Eq. 17).[157]



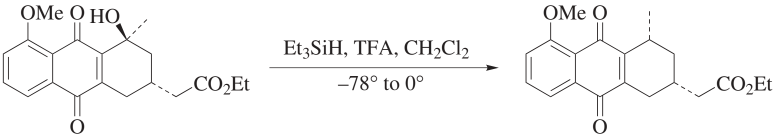
13 **14** (86%) (Eq. 17)

Several sterically congested aryldiadamantylmethanols are reduced to atropisomeric diastereomeric mixtures of the corresponding aryldiadamantylmethanes with Et_3SiH/TFA (Eq. 18).[158–161]



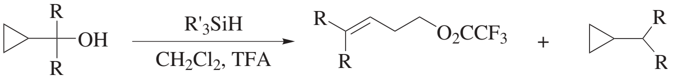
(—) 1:1 (Eq. 18)

This reagent combination reduces a tertiary alcohol in the presence of a quinone moiety (Eq. 19).[162] Tertiary alcohols are also reduced with the reagent combinations $Et_3SiH/MeSO_3H$[140] and $Et_3SiH/AlCl_3/HCl$.[136]



(95%) (Eq. 19)

Cyclopropylcarbinols. Treatment of cyclopropylcarbinols **15** (R = Ph, *c*-C_3H_5) with trifluoroacetic acid in dichloromethane leads to the rapid formation of ring-opened 4-substituted 3-butenyl-1-trifluoroacetate esters **16** (Eq. 20).[130] Cyclopropylcarbinyl trifluoroacetates are not formed. Ring opening is facilitated by phenyl substituents. Addition of organosilicon hydrides to the reaction mixture favors the formation of cyclopropylmethanes **17** and suppresses the formation of the ring-opened esters.[130]



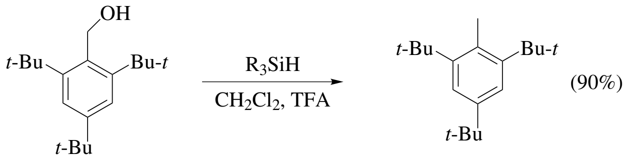
15 **16** **17** (Eq. 20)

R = *c*-C_3H_5	R' = Et	**16** + **17** (—), **16**:**17** = 1:99
R = Ph	R' = Et	**16** + **17** (—), **16**:**17** = 19:81

Triethylsilane and diethylsilane are somewhat more effective than triphenylsilane at increasing the amount of reduced product **17**.[130] Yields of **17** in excess of 90% may be obtained. The remainder of the product is butenyl ester **16**. Hydrogenolysis of the cyclopropyl rings does not occur under these conditions. A better yield of **17** is obtained when the reaction is carried out at −15° than at room temperature. Under the same set of reaction conditions (dichloromethane, 0.5 M trifluoroacetic acid, 0.5 hour, room temperature), the amount of hydrocarbon product **17** (R = Ph) obtained from diphenylcyclopropylcarbinol changes from 16% with triphenylsilane as the hydride-donating reagent to 45% with triphenylgermane, 85% with triphenylstannane, and 78% with tri-*n*-butylstannane.[24]

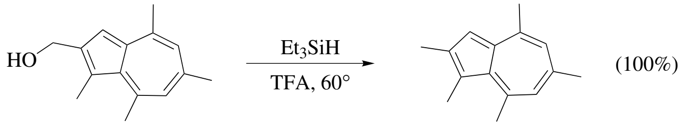
Benzyl Alcohols. Benzyl alcohols of nearly all kinds undergo reduction when treated with acid in the presence of organosilicon hydrides. The most obvious exception to this is the behavior of benzyl alcohol itself. It resists reduction by the action of trifluoroacetic acid and triethylsilane, even after extended reaction times.[26] Reducing systems consisting of triethylsilane and sulfuric acid/acetic acid or *p*-toluenesulfonic acid/acetic acid mixtures also fail to reduce benzyl alcohol to toluene.[134] As previously mentioned, substitution of boron trifluoride for trifluoroacetic acid results in the formation of modest yields of toluene, but only when a very large excess of the silane is used in order to capture the benzyl cation intermediate and suppress Friedel-Crafts oligomerization processes.[129,143]

Ring-substituted benzyl alcohols sometimes undergo such reduction more effectively than unsubstituted alcohols. For example, treatment of a dichloromethane solution of 2,4,6-trimethylbenzyl alcohol with trifluoroacetic acid and triphenylsilane produces a 41% isolated (89% by GLC) yield of isodurene.[26] Treatment of 2-methyl-4,6-di-*tert*-butylbenzyl alcohol with a three-fold excess of triethylsilane and trifluoroacetic acid in dichloromethane at room temperature gives an 85% yield of 2-methyl-4,6-di-*tert*-butyltoluene together with 15% of 3,5-di-*tert*-butyltoluene. The latter is presumably formed by loss of protonated formaldehyde from the C1 ring-protonated substrate.[128] Similar treatment of 2,4,6-tri-*tert*-butylbenzyl alcohol produces a 90% yield of 2,4,6-tri-*tert*-butyltoluene within one hour (Eq. 21).[128]



(Eq. 21)

The reduction of 2-(hydroxymethyl)-1,4,6,8-tetramethylazulene to 1,2,4,6,8-pentamethylazulene occurs quantitatively upon treatment with triethylsilane and trifluoroacetic acid at 60° for 19 hours (Eq. 22).[163]



(Eq. 22)

Treatment of either the cis or trans isomer of 4-*tert*-butyl-1-phenylcyclohexanol with trifluoroacetic acid and one of a variety of organosilicon hydrides in dichloromethane yields a mixture of *cis*- and *trans*-4-*tert*-butyl-1-phenylcyclohexane and the elimination product, 4-*tert*-butyl-1-phenylcyclohexene