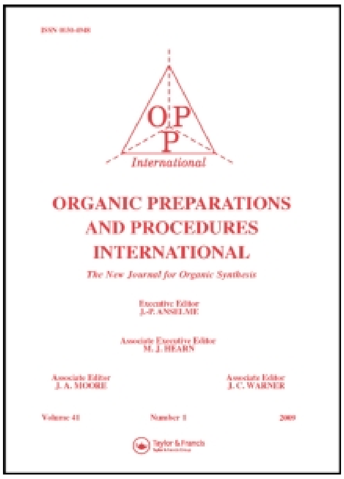
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HYDROSILANES AS REDUCING AGENTS. A REVIEW

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INTRODUCTION

The utility of organosilicon compounds such as silyl enol ethers, silyl-protected functional compounds, vinylsilanes, α,β-epoxysilanes, β-hydroxysilanes, allylsilanes, silylacetylenes, cyanosilanes, iodosilanes, azidosilanes and others to organic synthesis has been well documented.[1-11] Although the use of hydrosilanes as reducing agents has also received attention, this method still remains less common. The purpose of this review is to provide an introduction to this newer reduction method.

Although silane (SiH_4) itself is spontaneously inflammable in air, methylsilane (CH_3SiH_3) and ethylsilane ($CH_3CH_2SiH_3$) are more stable and ignite only under special conditions. The di- and triorganosilanes are even more stable and many of such silanes have been safely distilled in air at temperatures above 200°. Table 1 lists physical properties of some representative hydrosilanes which have been utilized to reduce various organic compounds. It should be noted that these hydrosilanes can be purchased commercially.*

The hydrogen in the Si-H bonds is hydridic in character,

Table 1. Physical Properties of Hydrosilanes

Compound	bp, °C	mp, °C	n_D^{20}
SiH_4	-112	-185	—
H_2SiCl_2	8	-122	—
$HSiCl_3$	32	-128	1.402
$MeSiH_3$	-57	-157	—
$MeSiHCl_2$	42	-93	1.422
Me_2SiH_2	-20	-150	—
Me_3SiH	7	-136	—
Et_2SiH_2	56	-134	1.392
$MeHSi(OMe)_2$	61	—	1.360
$HSi(OMe)_3$	87	—	1.369
Et_2MeSiH	78	—	1.398
Et_3SiH	108	—	1.412
$HSi(OEt)_3$	132	—	1.337
$PhSiH_3$	120	—	1.513
$PhMeSiH_2$	140	—	1.506
$PhMe_2SiH$	157	—	1.500
Ph_2SiH_2	97/13 mm	—	1.580
Ph_2MeSiH	267	—	1.569
Ph_3SiH	—	44	—
$(MeHSiO)_n$	high boiling oil		—

as would be expected from the electronegativities of silicon (1.7) and hydrogen (2.1), thus silanes function as hydrogen transfer agents toward electrophilic species such as carbonium ions to give the corresponding C-H compounds. However, the ionic character in the Si-H bond is not large as that in the Li-H or in the Al-H bond and commonly used hydrosilanes such as those listed in Table 1 are soluble even in non-polar solvents.

The average bond energy values of the Si-H and C-H bonds (70 and 99 Kcal/mol, respectively)[12] suggests that the Si-H bond should be susceptible to hydrogen atom abstraction by carbon radicals. Thus, the dehalogenation reaction of alkyl halides with a hydrosilane under homolytic conditions can be explained in terms of the following chain mechanism.[13]

$$R\cdot + R'_3SiH \longrightarrow RH + R'_3Si\cdot \qquad [1]$$

$$R'_3Si\cdot + RX \longrightarrow R'_3SiX + R\cdot \ (X = Cl, Br) \qquad [2]$$

In contrast to the hydridic character of hydrogens attached to silicon in the majority of organic hydrosilanes, the hydrogen of trichlorosilane ($HSiCl_3$) appears to be slightly protonic, as shown by the following reaction.[14]

$$HSiCl_3 + Et_3N \longrightarrow SiCl_3^- + Et_3NH^+$$

In addition, the ability of hydrosilanes to add to various transition metal phosphine complexes through the rupture of the Si-H bonds,[15,16] coupled with the tendency of functional

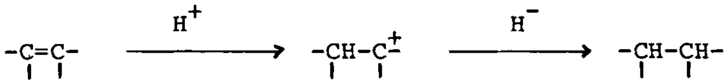
$$HSiCl_3 + RhCl(PPh_3)_3 \longrightarrow RhHCl(PPh_3)_2(SiCl_3) + PPh_3 \qquad [3]$$

groups of organic compounds to coordinate with transition metals, suggests that the combination of metal complexes and hydrosilanes might induce the redution of a variety of functional groups. The successful realization of this idea will be discussed in an appropriate section.

The aforementioned properties of hydrosilanes make it clear that the reduction of organic compounds with hydrosilanes often requires the use of a suitable activator. Nevertheless, the inertness of hydrosilanes toward moderately reducible environment in the absence of any added activator is convenient since this means that the reagents are rather safe to handle and can be stored without serious deterioration. Further, judicious choice of the activator can sometimes lead to selective reduction.

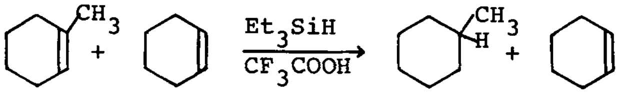
1. Reduction of Alkenes to Alkanes

The addition of hydrogen to alkenes is usually carried out at low temperatures and pressures in the presence of certain metals such as nickel, palladium and platinum. Catalytic hydrogenation of this type constitutes one of the most widely used methods in organic chemistry for the reduction of π-bonds. Recently, a new promising method, called "ionic hydrogenation",[17] has been developed; it often provides greater effectiveness and higher chemoselectivity.[18-30] The ionic hydrogenation of alkenes involves the protonation of the double bond forming the carbonium ion followed by the subsequent reaction with a hydride donor to give the hydrogenated product.



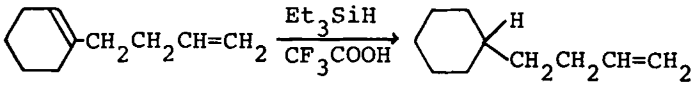
$$-\underset{|}{C}=\underset{|}{C}- \xrightarrow{H^+} -\underset{|}{C}H-\underset{|}{C}^{+} \xrightarrow{H^-} -\underset{|}{C}H-\underset{|}{C}H-$$ [4]

In these reactions, the hydrogenation pair consists of a proton donor and a hydride donor; among several possibilities, the pairs involving trifluoroacetic acid and organohydrosilanes have proved most useful. A variety of hydrosilanes can be used for the hydrogenation, but in many cases the use of triethylsilane (Et_3SiH) is convenient. As expected from the postulated mechanism involving the carbonium ion intermediate, alkenes branched at alkenyl carbon react with the trifluoroacetic acid-hydrosilane combination more rapidly than unbranched alkenes. For instance, reduction of a mixture of 1-methylcyclohexene and cyclohexene with a limited amount of Et_3SiH gives methylcyclohexane, and cyclohexene is recovered.[17]



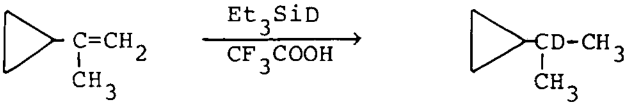
[5]

Competition between branched and unbranched double bonds in dienes leads to selective hydrogenation of the more branched double bond.[17]



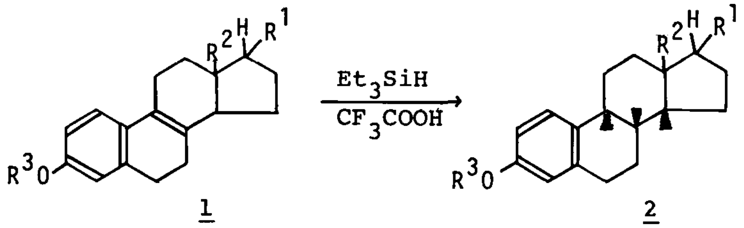
[6]

The carbonium ion intermediate can be intercepted with deuterium with a deuteride ion donor such as Et_3SiD to form the labeled hydrogenation product. Since the hydrogen isotope exchange reaction are not observed under the conditions employed, the reaction with the trifluoroacetic acid-triethyldeuterosilane combination opens a synthetic route to compounds having deuterium label in a predetermined position. For example, 2-D-2-cyclopropylpropane can be prepared in this fashion.[17]



[7]

The difference in stereochemistry for the addition of hydrogen to alkenes between the catalytic and the ionic hydrogenations is noteworthy. Catalytic hydrogenation often results in cis-addition of hydrogen to the double bonds. By contrast, predominant trans stereochemistry is often observed in ionic hydrogenation. As an example, the trifluoroacetic acid-triethylsilane combination reacts with 1,2-dimethylcyclopentene at 20° to give cis- and trans-isomers of 1,2-dimethylcyclpentane in a cis:trans ratio of 1:12.[17] The stereoselectivity of ionic hydrogenation coupled with the inertness of various functionalities such as -COOH, -COOR, $-CONR_2$, -CN, -OH and C-Hal groups, is synthetically useful for the hydrogenation of steroids.[17] As a typical example, dehydrosteroids such as (1a)-(1c) containing $\Delta^{8(9)}$ or $\Delta^{9(11)}$ double bonds undergo ionic hydrogenation to form derivatives of estradiol (2) with the natural trans-anti-trans-configuration in 56-60% yields.



[8]

a R^1 = OH, R^2 = R^3 = CH_3, $\Delta^{8(9)}$
b R^1-H = O, R^2 = R^3 = CH_3, $\Delta^{8(9)}$
c R^1 = OH, R^2 = R^3 = CH_3, $\Delta^{9(11)}$

2. Reduction of Alkynes to Alkenes

Acetylenic compounds readily add hydrosilanes to give silylethenes which yield in turn the corresponding ethylenic compounds regiospecifically through desilylation by hydroiodic acid. Thus, the overall reaction constitutes the partial hydrogenation of acetylenes to the corresponding olefins. Hydrosilylation (addition of a hydrosilane to a multiple bond) is readily catalyzed by a small amount of chloroplatinic acid (H_2PtCl_6) or Pt-C, and proceeds with cis-stereochemistry (and eventually the trans-olefins).[31] On the other hand, predominantly trans-hydrosilylation can be achieved by peroxide catalysts[31] or, in some cases, rhodium

$$-C{\equiv}C- \;+\; R_3SiH \longrightarrow -CH{=}C(SiR_3)- \xrightarrow{HI} -CH{=}CH- \qquad [9]$$

catalysts.[32,33] These stereoselective hydrosilylation combined with the regiospecific replacement of the silyl group by hydrogen or deuterium can thus lead to stereo- and regioselective preparation of alkenes or deuterated alkenes.[34]

3. Dehalogenation of Haloalkanes

Simple alkyl halides can be dehalogenated in the gas phase with a hydrosilane under irradiation.[35-38] The reaction can be understood in terms of a radical chain mechanism involving alternate formation of carbon and silyl radicals (Eq. 1 and 2). In the liquid phase, homolytic dehalogenation of monohaloalkanes is difficult to achieve at moderate temperatures, but partial dehalogenation of geminal polyhalides takes place readily with peroxide catalysis.[39-46] Thus, carbon tetrachloride gives chloroform in good yield when treated with triethylsilane in the presence of benzoyl peroxide at 80°.

$$CCl_4 + Et_3SiH \xrightarrow{BPO} CHCl_3\ (96\%) + Et_3SiCl \qquad [10]$$

The partial reduction of polyhaloalkanes is also effectively catalyzed by soluble metal complexes such as dichlorotris(triphenylphosphine)ruthenium(II).[47a]

$$CH_3(CH_2)_5CHClCH_2CCl_3 \xrightarrow[RuCl_2(PPh_3)_3]{Et_3SiH,\ 110°} \underset{(95\%)}{CH_3(CH_2)_5CHClCH_2CCl_3} \qquad [11]$$

Several workers[47b,48-51] have shown that other species including palladium chloride, chloroplatinic acid and Lewis acids catalyze the reduction of alkyl halides with hydrosilanes, but the reaction did not appear useful as a synthetic procedure because of the often complex nature of reduction products. However, in 1976, Doyle and coworkers[22] introduced a successful procedure for the reduction of various primary alkyl halide with a hydrosilane using aluminum chloride at low temperatures.

$$c\text{-}C_6H_{11}Cl + Et_3SiH \xrightarrow[0°,\ in\ C_5H_{12}]{cat.\ AlCl_3} c\text{-}C_6H_{12}(72\%) + Et_3SiCl \qquad [12]$$

The partial dehalogenation of geminal polyhalides can also be accomplished by an amine-catalyzed reaction with trichlorosilane.[14] In these reactions, the ratio of the reactants is

$$CCl_4 + HSiCl_3 \xrightarrow{cat.\ Bu_3^nN} CHCl_3(82\%) + SiCl_4 \qquad [13]$$

$$CCl_3COOMe + HSiCl_3 \xrightarrow{cat.\ Bu_3^nN} CHCl_2COOMe\ (82\%) + SiCl_4 \qquad [14]$$

very important.[52,53] When a full equivalent of the tertiary amine was employed, the halogens are replaced by a trichlorosilyl group rather than by hydrogen.

$$CCl_4 \xrightarrow[excess\ (n\text{-}C_3H_7)_3N]{HSiCl_3} CH_2(SiCl_3)_2 \qquad [15]$$

4. Reduction of Aldehydes and Ketones

Phenylsilanes add to benzophenone at temperatures of 220-270°.[54]

$$PhSiH_3 + Ph_2C{=}O \xrightarrow{250°} Ph_2CHOSiH_2Ph + (Ph_2CHO)_2SiHPh \qquad [16]$$

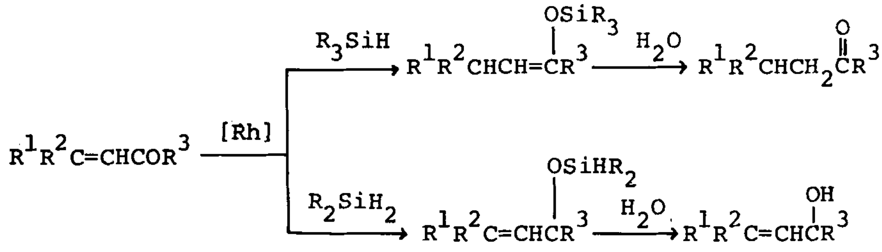
Under ultraviolet irradiation, a similar reaction occurs between trichlorosilane and aliphatic ketones.[55] The hydrosilylation of ketones and aldehydes is also effected by reduced metals or Lewis acids.[56-63] Since the resulting alkoxysilanes can readily be hydrolyzed to alcohols, these reactions may constitute a route for reducing ketones and aldehydes to alcohols. However, this type of hydrosilylation suffers from significant side-reactions.

Recently, it has been shown that the hydrosilylation of ketones and aldehydes can be effectively catalyzed by a homogeneous phosphine complex of rhodium, tris(triphenylphosphine)-chlororhodium(I).[64-69]

$$CH_3CH_2CH_2CHO + PhMeSiH_2 \xrightarrow[\text{rt, 5 min}]{RhCl(PPh_3)_3} \underset{(98\%)}{CH_3CH_2CH_2CH_2OSiHMePh} \qquad [17]$$

Similar complexes of ruthenium[67-69] and platinum[70] are also effective. In these reactions, the yields of alcohols (after hydrolysis) are exceedingly high and work-up procedures are very simple.

The rhodium(I)-catalyzed hydrosilylation of α,β-unsaturated carbonyl compounds with mono-hydrosilanes generally proceeds *via* a 1,4-addition, while dihydrosilanes tends to give silylated allylic alcohols.[71]



[18]

Hydrolysis of the resulting silyl enol ethers and allylic silyl ethers gives saturated carbonyl compounds and allylic alcohols, respectively, and therefore these reactions furnish a unique method for selective reduction of olefinic ketones and aldehydes.

Stereoselective reduction of terpene ketones can be achieved *via* the Rh(I)-catalyzed hydrosilylation.[72] Thus, the reaction of menthone with the less crowded phenylsilane gives a mixture of neomenthol and menthol in a ratio of 90/10, while the reaction with the more crowded phenyldimethylsilane gives menthol, which is more stable than neomenthol, exclusively. The stereoselectivity exhibited by the Rh(I)-catalyzed hydrosilane reduction producing more stable alcohols with bulky hydrosilanes is quite striking; reductin of camphor with a bulky hydroborane, diisopinocamphenylborane, gives the corresponding less stable alcohol exclusively.[73]

Asymmetric reductive hydrosilylation[74] of various carbonyl compounds is possible using platinum[75,76] and rhodium[77-87] complexes with chiral phosphine ligands as catalyst. Representative is the reaction of n-butyl pyruvate with α-naphtylphenylsilane in the presence of [(+)DIOP]Rh(S)Cl which affords the corresponding (S)-alcohol in 83% enantiomeric excess.

$$CH_3COCOOBu^n + \alpha\text{-}NpPhSiH_2 \xrightarrow{[Rh^*]} \xrightarrow{MeOH} \underset{(83\%\ ee)}{CH_3C^*HOHCOOBu^n} \qquad [19]$$

The reaction of the trifluoroacetic acid-organosilane combination with aliphatic ketones affords the corresponding secondary alcohols in good yield.[17] However, ionic hydrogenation of aliphatic aldehydes affords not only the alcohols but also the ethers as by-products. In addition, aromatic ketones and aldehydes generally give the corresponding hydrocarbons rather than the alcohols. These reactions are illustrated by the following examples.

$$CH_3COCH_2CH_3 \xrightarrow[CF_3COOH]{Et_3SiH} \underset{(80\%)}{CH_3CHOHCH_2CH_3} + \underset{(10\%)}{Bu^nOBu^n} \qquad [20]$$

$$C_2H_5CHO \longrightarrow \underset{(60\%)}{C_3H_7OH} + \underset{(38\%)}{Pr^nOPr^n} \qquad [21]$$

$$PhCOCH_3 \longrightarrow \underset{(70\%)}{PhCH_2CH_3} \qquad [22]$$

$$\underline{p}\text{-}MeOC_6H_4CHO \longrightarrow \underset{(30\%)}{\underline{p}\text{-}MeOC_6H_4CH_3} \qquad [23]$$

$$\mathrm{PhCOPh} \longrightarrow \underset{(94\%)}{\mathrm{PhCH_2Ph}} \qquad [24]$$

Fry and coworkers[88] found that effective reduction of aldehydes and ketones can be accomplished with an organosilane-boron trifluoride system. Examples are given below.

$$\underline{p}\text{-}\mathrm{NCC_6H_4CHO} \xrightarrow[\mathrm{BF_3}]{\mathrm{Et_3SiH}} \underset{(100\%)}{\underline{p}\text{-}\mathrm{NCC_6H_4CH_2OH}} \qquad [25]$$

$$\underline{p}\text{-}\mathrm{O_2NC_6C_4CHO} \xrightarrow[\mathrm{BF_3}]{\mathrm{Et_3SiH}} \underset{(100\%)}{\underline{p}\text{-}\mathrm{O_2NC_6H_4CH_2OH}} \qquad [26]$$

$$\mathrm{CH_3(CH_2)_9CHO} \xrightarrow[\mathrm{BF_3}]{\mathrm{Et_3SiH}} \underset{(92\%)}{\mathrm{CH_3(CH_2)_9CH_2OH}} \qquad [27]$$

It is significant that this method gives toluene from benzaldehydes since other acid-silane systems do not[17,21]; however, the yield (52%) is only moderate.

Commercially available polymethylhydrosiloxanes, in the presence of an organotin catalyst (dibutyltin acetate) in protic solvents, reduce aldehydes and ketones to carbinols selectively in high yield under mild and neutral conditions.[89] Under the conditions employed, ethers, lactones, amides,

$$\mathrm{RR'CO} + 1/n\mathrm{(MeHSiO)_n} \xrightarrow[\mathrm{EtOH}]{\mathrm{Bu^n_2Sh(OAc)_2}} \mathrm{RR'CHOH} \qquad [28]$$

carboxylic acids, nitriles, alkyl halides and nitro compounds are not reduced. The reactions seems to be suitable for large-scale preparation because of accessibility of siloxanes and the simplicity of the procedures.

The true entity of the active reducing agent in the system is likely to be a tin hydride as depicted by the following scheme.

$$\mathrm{SnOAc} + \mathrm{SiH} \longrightarrow \mathrm{SnH} + \mathrm{SiOAc}$$

$$\mathrm{SnH} + \mathrm{RR'CO} \longrightarrow \mathrm{RR'CHOSn}$$

$$\mathrm{RR'CHOSn} + \mathrm{EtOH} \longrightarrow \mathrm{RR'CHOH} + \mathrm{SnOEt}$$

$$\mathrm{SnOEt} + \mathrm{SiH} \longrightarrow \mathrm{SnH} + \mathrm{SiOEt}$$

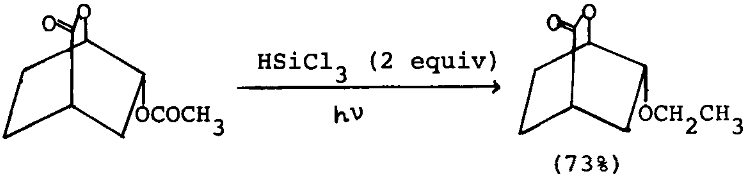
Use of a palladium-on-charcoal as catalyst compeletely alters the course of the reaction; nitrobenzene is thus reduced to aniline with polymethylhydrosiloxane-palladium system in 89% yield.

5. Reduction of Carboxylic Esters to Ethers

Tsurugi and coworkers[90-92] found that simple aliphatic esters can be reduced to the corresponding ethers upon irradiation with trichlorosilane. The yields are often

$$\mathrm{RCOOR'} \xrightarrow[h\nu]{\mathrm{HSiCl_3}} \mathrm{RCH_2OR'} \qquad [29]$$

quantitative. The applicability of the method to the reduction of more complex bicyclic lactones was also demonstrated.[93,94]



[30]

However, carboxylic esters containing an aryl group in either R or R' of RCOOR' are not reduced. The irradiation-initiated deoxygenation is accounted for in terms of the following mechanism in which the inertness of aryl compounds is ascribed to homolytic silylation of aromatic nucleus.

$$Cl_3Si\cdot + RCOOR' \longrightarrow R\dot{C}(OSiCl_3)OR'$$

$$R\dot{C}(OSiCl_3)OR' + HSiCl_3 \longrightarrow RCH(OSiCl_3)OR' + Cl_3Si\cdot$$

$$RCH(OSiCl_3)OR' + HSiCl_3 \longrightarrow RCHClOR' + HCl_2SiOSiCl_3$$

$$RCHClOR' + HSiCl_3 \longrightarrow RCH_2OR' + SiCl_4$$

$$Cl_3Si\cdot + PhH \longrightarrow \longrightarrow PhSiCl_3$$

6. Reductive Silylation of Carbonyl Compounds

The trichlorosilane-tertiary amine combinations can remove a carbonyl oxygen from aromatic ketones, aldehydes, acid chlorides, acid amides and aromtic acid.[14] Such a transformation is termed "reductive silylation" which can be represented as the replacement of a carbonyl oxygen by the H and $SiCl_3$ moieties of trichlorosilane.

$$RCOX \xrightarrow[R_3N]{HSiCl_3} RCH(SiCl_3)X \quad (X = \text{alkyl, H, } NR_2) \qquad [31]$$

Acid chlorides are converted into 1,1-bis(trichlorosilyl) compounds, while aromatic acids and their anhydrides can be reduced to benzylic silanes. Since the C-Si bonds in benzylic silanes can be cleaved by base, the overall sequence constitutes a very unique method for reducing aromatic carbonyl compounds. Examples below illustrate this reaction with aldehydes, ketones, amides and acids.[95-97]

$$2,6\text{-}Cl_2C_6H_3CHO \xrightarrow[Pr^n_3N]{HSiCl_3} \xrightarrow[KOH]{EtOH} \underset{(54\%)}{2,6\text{-}Cl_2C_6H_3CH_3} \qquad [32]$$

$$PhCOPh \xrightarrow[Pr^n_3N]{HSiCl_3} \xrightarrow[KOH]{EtOH} \underset{(72\%)}{PhCH_2Ph} \qquad [33]$$

$$\underline{p}\text{-}MeOC_6H_4CONMe_2 \xrightarrow[Pr^n_3N]{HSiCl_3} \xrightarrow[KOH]{EtOH} \underset{(55\%)}{\underline{p}\text{-}MeOC_6H_4CH_2NMe_2} \qquad [34]$$

$$\underline{p}\text{-}ClC_6H_4COOH \xrightarrow[Pr^n_3N]{HSiCl_3} \xrightarrow[KOH]{EtOH} \underset{(94\%)}{\underline{p}\text{-}ClC_6H_4CH_3} \qquad [35]$$

7. Reduction of Carboxylic Acid Halides to Aldehydes

Acyl halides had been reported to react with triorganohydrosilanes in ether to give aldehydes,[98] but this claim has been questioned.[99] Nevertheless, it has been recently shown that the chlorine-hydrogen exchange reaction between an acyl chloride and triethylsilane does occur in the presence of a variety of metal catalysts such as Pd-C,[100] $RhCl(CO)(PR_3)_2$, $PtCl_2(PR_3)_2$, $RuCl_2(PR_3)_3$ and $IrCl(CO)(PR_3)_2$.[101-103] The complex-catalyzed reduction, an alternative Rosenmund reduction, is illustrated by the following examples in which *cis*-$[PtCl_2(PPh_3)_2]$ was used as catalyst.

$$\underline{p}\text{-}MeOC_6H_4COCl + Et_3SiH \longrightarrow \underline{p}\text{-}MeOC_6H_4CHO \quad (65\%) \qquad [36]$$

$$\underline{p}\text{-}BrC_6H_4COCl + Et_3SiH \longrightarrow \underline{p}\text{-}BrC_6H_4CHO \quad (84\%) \qquad [37]$$

$$\underline{p}\text{-}O_2NC_6H_4COCl + Et_3SiH \longrightarrow \underline{p}\text{-}O_2NC_6H_4CHO \quad (78\%) \qquad [38]$$

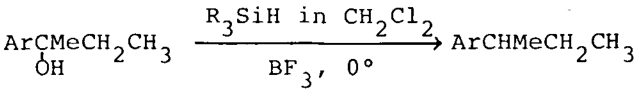
$$PhCH{=}CHCOCl + Et_3SiH \longrightarrow PhCH{=}CHCHO \quad (65\%) \qquad [39]$$

These reactions can be explained by the following catalytic cycle.

$$\begin{tikzcd}
L_2PtCl_2 \arrow[r, "Et_3SiH"] & L_2PtHCl_2(SiEt_3) \arrow[d, "-Et_3SiCl"] \\
L_2PtHCl_2(COR) \arrow[u, "-RCHO"] \arrow[r, leftrightarrow, "RCOCl"] & L_2PtHCl
\end{tikzcd}$$

8. Reduction of Alcohols to Alkanes

Since the principle of ionic hydrogenation[17] relies on the trapping of the carbonium ion by hydride transfer, alcohols which can form carbonium ions readily are susceptible to reduction with various hydrogenating pairs. Such alcohols include tertiary aliphatic alcohols, tertiary and secondary benzyl alcohols, cyclopropyl alcohols and primary benzyl alcohols with strongly electron-releasing substituents on the aromatic ring. Thus, triethylcarbinol, trityl alcohol, benzhydryl alcohol, bis(cyclopropyl)carbinol, 2,4,6-trimethylbenzyl alcohol, all give the corresponding alkanes in good yields (70-100%) when treated with the trifluoroacetic acid-organosilane combinations. However, there exist at least two general sets of conditions under which the use of trifluoroacetic acid to generate the required carbonium ions from alcohol precursors is unsatisfactory. These include alcohols which suffer rapid skeletal rearrangement and/or elimination upon contact with the protic acid or alcohols which do not readily yield a sufficient concentration of carbonium ions when treated with protic acids. Such difficulties can be overcome by the use of gaseous boron trifluoride in place of protic acids. Thus, dichloromethane solutions of a number of alcohols and silanes undergo facile reactions to form the corresponding hydrocarbons when boron trifluoride is passed into the solution.[104]



$$\mathrm{Ar\underset{OH}{C}MeCH_2CH_3} \xrightarrow[\mathrm{BF_3,\ 0^\circ}]{\mathrm{R_3SiH\ in\ CH_2Cl_2}} \mathrm{ArCHMeCH_2CH_3} \qquad [40]$$

The ionic hydrogenation of alcohols often gives rise to other difficulties, especially when other reducible groups such as carbonyl are present. Jackson and coworkers[105] have recently presented a novel method for the successful

$$ROH \xrightarrow{COCl_2} ROCOCl \xrightarrow[peroxide]{Pr_3SiH} RH + CO_2 + Pr_3SiCl \qquad [41]$$

reduction of alcohols to the corresponding alkanes; the alchols is first converted to alkyl chloroformate followed by treatment with a hydrosilane in the presence of di-t-butyl peroxide. The selectivity of the reaction is promising since a 69% yield of pentan-2-one from $CH_3COCH_2CH_2OH$ was obtained.

9. Reduction of Imines to Amines

The hydrosilylation of imines in the presence of Wilkinson's catalyst ($RhCl(PPh_3)_3$) affords the corresponding silylated amines in virtually quantitative yields.[106,107]

$$PhCH{=}NMe + Et_2SiH_2 \xrightarrow[30°,\ 30\ min]{[Rh]} \underset{(95\%)}{PhCH_2NMe(SiEt_2H)} \qquad [42]$$

$$Ph_2C{=}NH + Et_2SiH_2 \xrightarrow[50°,\ 10\ min]{[Rh]} \underset{(98\%)}{Ph_2CHNH(SiEt_2H)}$$

Desilylation of the resulting N-silylamines can be easily accomplished by methanolysis. The hydrosilylation of Schiff bases can be also catalyzed by Lewis acids or by other complexes,[108,109] but the Rh(I) complex seems to be the catalyst of choice because of the ease of the reaction and of the work-up.

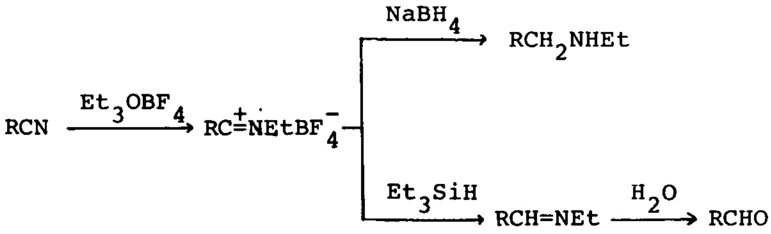
An effective asymmetric hydrosilylation reduction of imines to optically active amines using Rh(I) catalysts with chiral ligands has been reported to give enantiomeric excess of up to 65%.[110]

The ionic hydrogenation[17] is also successful with aromatic azomethines but not with aliphatic Schiff bases.

$$\mathrm{PhCH{=}NPh} \xrightarrow[60-70^\circ]{\mathrm{CF_3COOH/Et_3SiH}} \underset{(80\%)}{\mathrm{PhCHNHPh}}$$

10. Reduction of Nitriles to Imines or Aldehydes

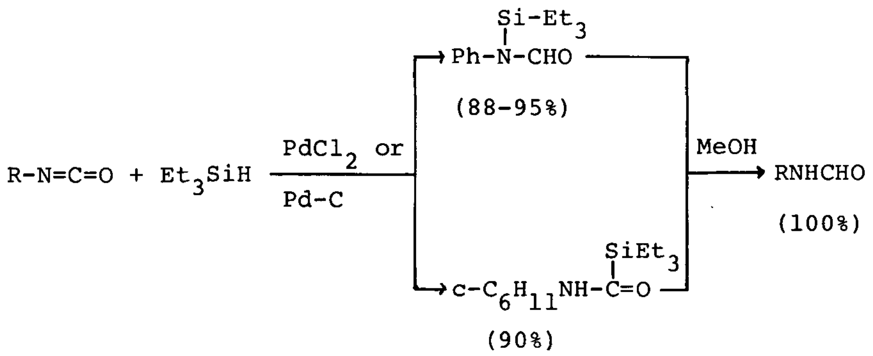
Although nitriles resist reduction by sodium borohydride, this reagent readily reduces N-alkylnitrilium ions prepared from nitrile and triethyloxonium tetrafluoroborate to the corresponding secondary amines in high yields.[111] An attempt to halt reduction at the imine stage was reported to be unsuccessful. Fry[112] found that an N-ethylnitrilium tetrafluoroborate reacts with triethylsilane in dichloromethane solution at room temperature to give aldehydes in good yields after hydrolysis. Representative overall yields of aldehydes are R = Bu, 71%; Pr^i, 85%; Bu^t, 61%; 1-adamantyl, 83%; cyclopropyl, 79%; $PhCH_2$, 41%; Ph, 90%; 1-naphthyl, 84%.



[43]

11. Reduction of Heterocumulenes

The hydrosilylation of isocyanates is promoted by palladium dichloride or Pd-C to give N-silylformamides or C-silylamides, depending upon the structure of isocyanates.[113] Upon methanolysis, however, the intermediates give formamides.

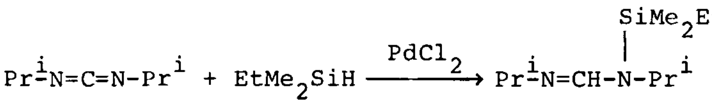


$$R{-}N{=}C{=}O + Et_3SiH \xrightarrow[\text{Pd-C}]{\text{PdCl}_2\text{ or}} \left\{ \begin{array}{l} Ph{-}\overset{Si-Et_3}{N}{-}CHO\ (88\text{-}95\%) \\ c{-}C_6H_{11}NH{-}\overset{SiEt_3}{C}{=}O\ (90\%) \end{array} \right\} \xrightarrow{MeOH} RNHCHO\ (100\%)$$

[44]

Consequently, the hydrosilylation of isocyanates followed by methanolysis of the adducts provides a convenient method for the reduction of isocyanates to formamides. It should be noted that the lithium aluminum hydride reduction of isocyanates gives methylamines rather than formamides.

By contrast, the hydrosilylation of carbodiimides[114,115] affords N-silylformamidines exclusively; the formation of C-silylated amidines is not observed.



$$Pr^i{-}N{=}C{=}N{-}Pr^i + EtMe_2SiH \xrightarrow{PdCl_2} Pr^i{-}N{=}CH{-}\overset{SiMe_2Et}{N}{-}Pr^i$$

[45]

The reaction is also catalyzed by rhodium(I) complexes. The N-silylformamidines react exothermally with water or methanol to give formamidines quantitatively and thus the hydrosilylation of carbodiimides followed by hydrolysis furnishes a facile route to formamidines.

12. Deoxygenation of Phosphine Oxides

Fritzsche and coworkers[116,117] found that various hydrosilanes reduce phosphine oxides to phosphines in good to excellent yields.

$$Ph_3PO \xrightarrow[120°]{PhSiH_3} Ph_3P \quad (82\%)$$

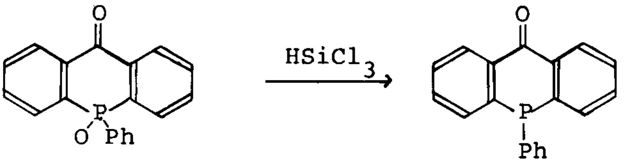
$$Ph_3PO \xrightarrow[PhH,\ 80°]{HSiCl_3} Ph_3P \quad (98\%)$$

$$PhP(O)(OEt)_2 \xrightarrow{Ph_2SiH_2} PhPH_2 \quad (87\%)$$

This finding has been confirmed by others.[118-128]

In 1974, Marsi[126] reported the use of phenylsilane to reduce one isomer of 1,3-dimethylphospholane 1-oxide with complete retention of configuration. Since a variety of stereochemically pure phosphine oxides are available, this method provides a convenient route to stereochemically pure phosphines. In addition to satisfactory yields and clean stereochemistry, there are some other advantages to the use of phenylsilane. For example, the reaction is normally carried out by simply mixing the phosphine oxide in the absence of solvent. Since phenylsilane is reasonably volatile and the siloxane polymers formed as by-products are nonvolatile, the phosphines are obtained by simple distillation.

Phosphine oxides appear to be more reactive than ketones toward trichlorosilane and thus heating the ketophosphine oxide depicted in eq. 46 with an excess of trichlorosilane in benzene at reflux yielded the ketophosphine in 90% yield.[127]



[46]

13. Reduction of Sulfur Compounds

Chan and coworkers[129] reported that aromatic sulfoxides can be reduced by an excess of trichlorosilane in ether to give the corresponding sulfides in high yields.

$$Ar_2S{=}O \xrightarrow{HSiCl_3} \underset{(85\text{-}100\%)}{Ar_2S} \qquad [47]$$

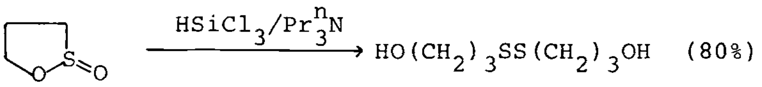
However, under identical conditions aliphatic sulfoxides are converted to mercaptals and sulfides.

$$(RCH_2)_2S{=}O \xrightarrow{HSiCl_3} RCH(SCH_2R)_2 + (RCH_2)_2S \qquad [48]$$

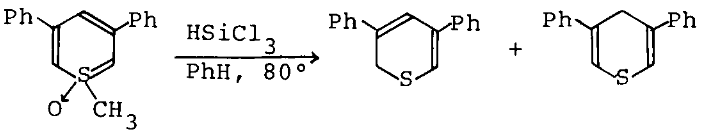
The tri-n-propylamine-trichlorosilane system reduces various sulfur compounds such as sulfenyl, sulfinyl and sulfonyl chlorides as well as sulfenate and sulfinate esters to the corresponding symmetrical disulfides. The following examples illustrate the reaction.[130]

$$PhSO_2Cl \xrightarrow{HSiCl_3/Pr^n_3N} PhSSPh \quad (85\%)$$

$$p\text{-}MeC_6H_4SO_2Cl \xrightarrow{HSiCl_3/Pr^n_3N} p\text{-}MeC_6H_4SSC_6H_4Me\text{-}p \quad (91\%)$$

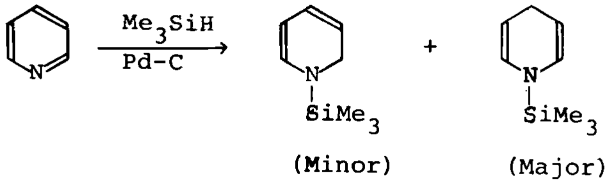


Reduction of a thiabenzene 1-oxide with 1 mol eqiv of trichlorosilane in refluxing benzene was reported to afford a 3:2 mixture of 2-H- and 4-H-thiapyrans.[131]



14. Miscellaneous

Cook and Lyons reported that pyridines add trimethylsilane in the presence of Pd-C, Rh-C and $PdCl_2$ yielding a variety of N-trimethylsilyl 1,2- and 1,4-dihydropyridines.[132] Under equilibrium conditions, the 1,4-addition products predominate. Since N-trimethylsilyl species can be converted into the parent dihydropyridines by hydrolysis, the method provides a route to unsubstituted N-(H)-dihydropyridines which are otherwise inaccessible.



Simamura and coworkers[133] found that diazonium fluoroborates are reduced by triethylsilane in acetonitrile at room temperature to give the corresponding arenes, thus providing a route for replacement by hydrogen of the amino group attached to an aromatic nucleus.

$$ArN_2BF_4 + Et_3SiH \longrightarrow ArN{=}NH + BF_3 + Et_3SiF$$

$$ArN{=}NH \longrightarrow ArH + N_2$$

In these reactions, the participation of aryl radicals is implicated, as evidenced by the fact that some undeuterated benzenes were obtained from the reduction of the diazonium salts with tri-n-butyltin deuteride in solvents such as THF.

$$Ar\cdot + SH(Solvent) \longrightarrow ArH + S\cdot$$

$$Ar\cdot + Et_3SiH \longrightarrow ArH + Et_3Si\cdot$$

As mentioned in Section 4, the reduction of nitrobenzene with polymethylhydrosiloxanes add ethanol in the presence of Pd-C gives aniline in 89% yield. With this particular system, benzaldehyde gives toluene in 84% yield, while methyl vinyl ketone gives methyl ethyl ketone quatitatively.[89] Thus, reductions using polymethylhydrosiloxanes and Pd-C constitute a safe, convenient form of low-pressure hydrogenation. Although the observed pattern of the reductions is similar to those obtained with hydrogen and Pd-C at 1 atm and room temperature, the reaction does not proceed simply by the known Pd-C catalyzed solvolysis of silyl hydride, followed by olefin hydrogenation. This is implied by an observation that, in the reduction of 2-nonene containing a 75:23 mixture of *trans*-/*cis*-isomers, only the *cis*-isomer

$$SiH + ROH \longrightarrow SiOH + H_2$$

$$\text{olefin} + H_2 \longrightarrow \text{paraffin}$$

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