Triethylsilane\(^1\)

\[
\text{Et}_3\text{SiH}
\]

[617-86-7] \(\text{C}_6\text{H}_{16}\text{Si} \quad (\text{MW} 116.31)\)

InChI = 1/C6H16Si/c1-4-7(5-2)-6/h7H,4-6H2,1-3H3

InChIKey = AQRNLNPVMDITEJU-UHFFFAOYAL

(mild reducing agent for many functional groups)

**Physical Data:** mp \(-156.9^\circ\text{C}\); bp 107.7\(^\circ\text{C}\); d 0.7309 g cm\(^{-3}\).

**Solubility:** insol H\(_2\)O; sol hydrocarbons, halocarbons, ethers.

**Form Supplied in:** colorless liquid; widely available.

**Purification:** simple distillation, if needed.

**Handling, Storage, and Precautions:** triethylsilane is physically very similar to comparable hydrocarbons. It is a flammable, but not pyrophoric, liquid. As with all organosilicon hydrides, it is capable of releasing hydrogen gas upon storage, particularly in the presence of acids, bases, or fluoride-releasing salts. Proper precautions should be taken to vent possible hydrogen buildup when opening vessels in which triethylsilane is stored.

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**Original Commentary**

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**Introduction.** Triethylsilane serves as an exemplar for organosilicon hydride behavior as a mild reducing agent. It is frequently chosen as a synthetic reagent because of its availability, convenient physical properties, and economy relative to other organosilicon hydrides which might otherwise be suitable for effecting specific chemical transformations.

**Hydrosilylations.** Addition of triethylsilane across multiple bonds occurs under the influence of a large number of metal catalysts.\(^2\) Terminal alkenes undergo hydrosilylations easily with triethylsilane in the presence of platinum,\(^3\) rhodium,\(^3a, 4\) iridium,\(^5\) osmium,\(^6\) or iridium\(^4\) catalysts. For example, phenylacetylene can form three possible isomeric hydrosilylation products with triethylsilane; the \((Z)-\beta\)-, the \((E)-\beta\)-, and the \(\alpha\)-products (eq 1). The \((Z)-\beta\)-isomer is formed exclusively or preferentially with ruthenium\(^5\) and some rhodium\(^4\) catalysts, whereas the \((E)-\beta\)-isomer is the major product formed with platinum\(^3\) or iridium\(^4\) catalysts. In the presence of a catalyst and carbon monoxide, terminal alkenes undergo silylcarbonylation reactions with triethylsilane to give \((Z)-\) and \((E)-\)β-silylacryaldehydes.\(^7\) Phenylacetylene gives an 82\% yield of a mixture of the \((Z)-\) and \((E)-\)isomers in a 10:1 ratio when 0.3 mol \% of Dirhodium(II) Tetrakis (perfluorobutyrate) catalyst is used under atmospheric pressure at 0\(^\circ\text{C}\) in dichloromethane (eq 2).\(^7d\) Terminal alkenes react with triethylsilane in the presence of this catalyst to form either ‘normal’ anti-Markovnikov hydrosilylation products or allyl- or vinylsilanes, depending on whether the alkene is added to the silane or vice versa.\(^8\) A mixture of 1-hexene and triethylsilane in the presence of 2 mol \% of an iridium catalyst ([IrCl(CO)\(_2\)]\(_2\)) reacts under 50 atm of carbon monoxide to give a 50\% yield of a mixture of the \((Z)-\) and \((E)-\)enol silyl ether isomers in a 1:2 ratio (eq 3).\(^9\) Hydrolysis yields the derived acylsilane quantitatively.\(^9\)

\[
\begin{align*}
\text{Ph} & \quad \text{Et}_3\text{SiH} \quad \text{cat} \\
\text{H} & \quad \text{H} & \quad \text{H} & \quad \text{SiEt}_3 & \quad \text{Et}_3\text{Si} & \quad \text{H} \\
\text{Ph} & \quad \text{SiEt}_3 & \quad \text{Ph} & \quad \text{H} & \quad \text{SiEt}_3 & \quad \text{Et}_3\text{Si} & \quad \text{H} \\
\text{Ph} & \quad \text{SiEt}_3 & \quad \text{Ph} & \quad \text{H} & \quad \text{SiEt}_3 & \quad \text{Et}_3\text{Si} & \quad \text{H}
\end{align*}
\]

(eq 1)

\[
\begin{align*}
\text{Ph} & \quad \text{Et}_3\text{SiH} \quad \text{cat} \\
\text{H} & \quad \text{H} & \quad \text{SiEt}_3 & \quad \text{Et}_3\text{Si} & \quad \text{H} \\
\text{Ph} & \quad \text{SiEt}_3 & \quad \text{Ph} & \quad \text{H} & \quad \text{SiEt}_3 & \quad \text{Et}_3\text{Si}
\end{align*}
\]

(eq 2)

\[
\begin{align*}
\text{BuCH}=&\text{CH}_2 & \quad \text{Et}_3\text{SiH} & \quad \text{CO} & \quad \text{cat} \\
\text{Bu} & \quad \text{SiEt}_3 & \quad \text{Et}_3\text{Si} & \quad \text{H} & \quad \text{OSiEt}_3
\end{align*}
\]

(eq 3)

\[
\begin{align*}
\text{H} & \quad \text{H} & \quad \text{SiEt}_3 & \quad \text{Et}_3\text{Si} & \quad \text{H} \\
\text{Ph} & \quad \text{SiEt}_3 & \quad \text{Ph} & \quad \text{H} & \quad \text{SiEt}_3 & \quad \text{Et}_3\text{Si}
\end{align*}
\]

(eq 4)

\[
\begin{align*}
\text{H} & \quad \text{H} & \quad \text{SiEt}_3 & \quad \text{Et}_3\text{Si} & \quad \text{H} \\
\text{Ph} & \quad \text{SiEt}_3 & \quad \text{Ph} & \quad \text{H} & \quad \text{SiEt}_3 & \quad \text{Et}_3\text{Si}
\end{align*}
\]

(eq 5)

**Silane Alcoholysis.** Triethylsilane reacts with alcohols in the presence of metal catalysts to give triethylsilyl ethers.\(^17\) The use of dirhodium(II) perfluorobutyrate as a catalyst enables regioselective formation of monosilyl ethers from diols (eq 6).\(^{17a}\)

\[
\begin{align*}
\text{Bu} & \quad \text{OH} & \quad \text{Et}_3\text{SiH} \quad \text{Rhf[pfBu\(_3\)]} & \quad \text{cat} \\
\text{Bu} & \quad \text{SiEt}_3 & \quad \text{Et}_3\text{Si} & \quad \text{H}_2
\end{align*}
\]

(eq 6)

Avoid Skin Contact with All Reagents
Formation of Singlet Oxygen. Triethylsilane reacts with ozone at -78 °C in inert solvents to form triethyldihydrotrioxosilane, which decomposes at slightly elevated temperatures to produce triethysilanone and Singlet Oxygen. This is a convenient way to generate this species for use in organic synthesis.18

Reduction of Acyl Derivatives to Aldehydes. Aroyl chlorides and bromides give modest yields of aryl aldehydes when refluxed in diethyl ether with triethylsilane and Aluminum Chloride.19 Better yields of both alkyl and aryl aldehydes are obtained from mixtures of acyl chlorides or bromides and triethylsilane by using a small amount of 10% Palladium on Carbon catalyst (eq 7).20 This same combination of triethylsilane and catalyst can effect the reduction of ethyl thiol esters to aldehydes, even in sensitive polyfunctional compounds (eq 8).21

\[
\text{C}_7\text{H}_5\text{COCl} + \text{Et}_3\text{SiH} \xrightarrow{10\% \text{Pd/C}} \text{C}_7\text{H}_5\text{CHO} \quad (7)
\]

Radical Chain Reductions. Triethylsilane can replace toxic and difficult to remove organotin reagents for synthetic reductions under radical chain conditions. Although it is not as reactive as Tributylstannane,22 careful choice of initiator, solvent, and additives leads to effective reductions of alkyl halides,23,24 alkyl sulfides,23 and alcohol derivatives such as O-alkyl S-methyl dithiocarbonate (xanthate) and thionocarbonate esters.22,23,25,26 Portionwise addition of 0.6 equiv of Dibenzoyl Peroxide to a refluxing triethylsilane solution of O-cholestan-3β-yl O′-(4-fluorophenyl) thionocarbonate gives a 93% yield of cholestane (eq 9).22 The same method converts bis-xanthates of vic-diols into alkenes (eq 10).22 Addition of a small amount of thiol such as t-dodecanethiol to serve as a ‘polarity reversal catalyst’24 with strong radical initiators in nonaromatic solvents also gives good results.23,25 Treatment of ethyl 4-bromobutanoate with four equiv of triethylsilane, two equiv of dilauroyl peroxide (DLP), and 2 mol % of t-dodecanethiol in refluxing cyclohexane for 1 hour yields ethyl butanoate in 97% yield (eq 11).

\[
\text{Br} \xrightarrow{\text{Et}_3\text{SiH}, \Delta} \text{CO}_2\text{Et} \quad (11)
\]

Ionic Hydrogenations and Reductive Substitutions. The polar nature of the Si–H bond enables triethylsilane to act as a hydride donor to electron-deficient centers. Combined with Brønsted or Lewis acids this forms the basis for many useful synthetic transformations.27 Use of Trifluoromethanesulfonic Acid (triflic acid) at low temperatures enables even simple alkenes to be reduced to alkanes in high yields (eq 12).20 Boron Trifluoride monohydrate is effective in promoting the reduction of polycyclic aromatic compounds (eq 13).29 Combined with thiol,

A list of General Abbreviations appears on the front Endpapers
Triethylsilane in 3M ethereal Lithium Perchlorate solution effects the reduction of secondary allylic alcohols and acetates (eq 18). The combination of triethylsilane and Titanium(IV) Chloride is a particularly effective reagent pair for the selective reduction of acetals. Treatment of (±)-frontalin with this pair gives an 82% yield of tetrahydrofuran products with a cis:trans ratio of 99:1 (eq 19). This exactly complements the 1:99 product ratio of the same products obtained with Dioxobutylaluminum Hydride.

Triethylsilane and trityl salts or Trimethylsilyl Trifluoromethanesulfonate are effective for the reduction of various ketones and acetals, as are combinations of Chlorotrimethylsilane and indium(III) chloride and Tin(II) Bromide and Acetyl Bromide. Isophthaldehyde undergoes reductive polycondensation to a polyester when treated with triethylsilane and Triphenylmethyl Perchlorate.

Triethylsilane reduces nitrilium ions to aldimines, diazonium ions to hydrocarbons, and aids in the deprotection of amino acids. With aluminum halides, it reduces alkyl halides to hydrocarbons.

First Update

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Additional Hydroxylation.

Hydroxylation of terminal alkenes with triethylsilane (eq 1) have been improved in terms of their regio- and stereocontrol as well as in other aspects of their operation. Through the employment of Pt(DVDS), Pt-catalyzed hydroxylation of 1-alkynes can now be performed at room temperature and in water with very high selectivity for the (E)-β-vinylsilanes (eq 20). It has also been shown that PtO2 catalyzes the internal hydroxylation of aryl alkynes under ortho-substituent regiocontrol (eq 21). Strong preference for the (E)-β-vinylsilanes during the hydroxylation of 1-alkynes has also been observed with cationic Ru-catalysts and [RhCl(nbd)]2/ dppp, the latter of which can also be employed in water (eq 20). Hydroxylation affords α-vinylsilanes when catalyzed by [CpRu(MeCN)3]PF6 (eq 20). (Z)-β-Vinylsilanes are similarly made under [RuCl2(p-cymene)]2 catalysis or by the trans hydroxylation of 1-alkynes under Lewis acid (AlCl3) catalysis.

AlCl3 can also promote the hydroxylation of allenes and alkenes. With regard to the hydroxylation of allenes; Rh-catalyzed reactions of Et3SiH and methylenecyclopropanes provide a convenient route to homoallylic silanes.

The hydroxylation of carbonyl compounds with Et3SiH (eq 4) has also been the subject of additional research. Owing to these efforts, carbonyls can now be directly converted to their triethylsilyl (TES) ethers with copper catalysts in the company of a bidentate phosphine ligand. Triethylsilylethers can also be made from carbonyl compounds and Et3SiH in the presence of rhodium(V) o xo-complexes.

Additional Silane Alcoholysis.

The direct silylation of alcohols with triethylsilane (eq 26) continues to be an interesting, if somewhat underused, method to TES protect alcohols. Recent works have demonstrated that this process is promoted by a number of catalysts including PdCl2, a Au(I) catalyst, and the Lewis acid B(C6F5)3.

<table>
<thead>
<tr>
<th>R−OH</th>
<th>Et3SiH</th>
<th>R−OSiEt3</th>
<th>Catalyst % Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>1° and 2° aliphatic</td>
<td>PdCl2</td>
<td>78–98</td>
<td></td>
</tr>
<tr>
<td>1°, 2°, 3° aliphatic or Ar</td>
<td>Au(I)</td>
<td>80–100</td>
<td></td>
</tr>
<tr>
<td>2°, 3° aliphatic or Ar</td>
<td>B(C6F5)3</td>
<td>95–100</td>
<td></td>
</tr>
</tbody>
</table>

Avoid Skin Contact with All Reagents
Additional Ionic Hydrogenation and Reductive Substitutions.

Nitrogen Containing Functional Group Reductions. As previously discussed, triethylsilane can donate its hydride to carbonyls and other functional groups (eqs 12–19)\(^{27-43}\) A variety of transition metals have recently emerged as promoters of such reactions, especially for reductions of nitrogen containing moieties. For example, organic azides are efficiently transformed to reactions, especially for reductions of nitrogen containing moieties. For example, organic azides are efficiently transformed to their Boc-protected amines with catalytic palladium in the presence of di-tert-butyl dicarbonate (eq 24).\(^{62}\)

\[
\begin{align*}
\text{Ar} &\text{N} \quad \text{EtSiH} \\
\text{Me} &\text{SnCl}_2 \\
(0-91\%) &\text{cat Pd, BocO} \\
\text{R} &\text{N}_3 \\
\text{EtSiH} &\text{R} \rightarrow \text{Boc} \\
\text{R} &\text{N} \\
\text{H} &\text{cat} \\
\end{align*}
\]

(24)

Alternatively, if such azides bear a 1\(^\prime\)′-benzylic group they can be converted to N-methylanilines by reaction with Et\(_3\)SiH and SnCl\(_2\).\(^{63}\) Wilkinson’s catalyst and Et\(_3\)SiH reduce aromatic nitro groups to their amines in moderate to good yields,\(^{64}\) while the combination of Pd(OAc)\(_2\) and Et\(_3\)SiH in a THF–water mixture reduces aliphatic nitro groups to the N-hydroxylamines (eq 25).\(^{65}\)

\[
\begin{align*}
\text{R} &\text{NO}_2 \\
\text{EtSiH} &\text{cat} \\
\rightarrow &\text{R} \rightarrow \text{N} \\
\text{H} &\text{cat} \\
\end{align*}
\]

(25)

Imines are reduced by triethylsilane to their amines when the proper Ir\(^{66,67}\) or Ni\(^{68}\) catalysts are employed. Non-metal-mediated reductions of C=N groups by Et\(_3\)SiH are also possible. Among these, the trifluorosulphonic acid promoted reductive amidation of aliphatic and aromatic aldehydes with Et\(_3\)SiH is an excellent way to mono N-alkylate aliphatic and aromatic amides, thioamides, carbamates, and ureas (eq 26).\(^{69}\) It is also worth noting that trifluorosulphonic acid/Et\(_3\)SiH reduces acyl- and tosylhydrazones to hydrazides\(^{70,71}\) and 2-aminopyrimidines to 2-amino-dihydro-2-aminotetrahydropyrimidines (eq 27).\(^{72}\)

\[
\begin{align*}
\text{X} &\text{NH}_2 + \text{R}^1\text{CHO} \\
\text{EtSiH} &\text{TFA} \\
\xrightarrow{63-97\%} &\text{R}^1\text{NH} \\
\text{R}^2 &\text{N} \\
\end{align*}
\]

(26)

\[
\begin{align*}
\text{R}^1 &\text{N} \rightarrow \text{R}^1\text{NH} \\
\text{R}^2 &\text{N} \\
\text{EtSiH} &\text{TFA} \\
\rightarrow (60-90\%) &\text{R}^1\text{NH} \\
\text{R}^2 &\text{N} \\
\end{align*}
\]

(27)

Novel syntheses of amino acids have also employed triethylsilane C–O bond cleavages of N,O-acetals. In this way, N-methyl-amino acid derivatives are isolated in high yields from the Fmoc or Cbz protected 5-oxazolidinone precursors, using TFA and Et\(_3\)SiH\(^{78,79}\) or with the Lewis acid AlCl\(_3\) and Et\(_3\)SiH (eq 31).\(^{80}\) A one-pot preparation of N-methyl-α-amino acid dipeptides can be accomplished from an oxazolidinone, amino acid, TFA, and Et\(_3\)SiH combination.\(^{81}\)

**Reductive Etherifications and Acetal Reductions.** Additional applications of triethylsilane in the reduction of C–O bonds also continue to surface. The Kusanov–Parnes dehydrative reduction\(^{27}\) of hemiacetals and acetals with trifluorosulphonic acid/Et\(_3\)SiH has proven especially valuable. Under such conditions, 4,6-O-benzylidenecetac glucose derivatives can be asymmetrically deprotected to 6-O-benzyl-4-hydroxy derivatives (eq 28)\(^{73}\) and thioether derivatives can be converted to syn,2,3-bisaryl (or heteroaryl) dihydrobenzoxanths with excellent stereo- and chemoselectivity (eq 29).\(^{74}\) Triethylsilane is also useful in a number of related acetal reductions, including those used for the formation of C-glycosides. For example, Et\(_3\)SiH reductively opens 1,3-dioxolanes to 2-alkoxy carboxylic acids when catalyzed by TiCl\(_4\).\(^{75}\) Furthermore, functionalized tetrahydrofurans are generated in good yield from 1,2-O-isopropylidenefuranose derivatives with boron trifluoride etherate and Et\(_3\)SiH (eq 30).\(^{76}\) These same conditions lead to 1,4- or 1,5-anhydroalditols when applied to methyl furanosides or pyranosides.\(^{77}\)

\[
\begin{align*}
\text{R}^1 &\text{Ac, Bn; R}^2 = \text{OAc, OBn, NHAc} \\
\text{MeSi} &\text{TFA} \\
(80-95\%) &\text{R}^1 \\
\end{align*}
\]

(28)

\[
\begin{align*}
\text{R}^1 &\text{Ac, Bn; R}^2 = \text{OAc, OBn, NHAc} \\
\text{MeSi} &\text{TFA} \\
(30-95\%) &\text{R}^1 \\
\end{align*}
\]

(29)

\[
\begin{align*}
\text{CH}_2\text{OR} &\text{Bf}_3, \text{Et}_2\text{O} \\
\xrightarrow{72-95\%} &\text{CH}_2\text{OR} \\
\text{R}^1 &\text{O} \\
\text{O} &\text{R}^2 \\
\end{align*}
\]

(30)

A list of General Abbreviations appears on the front Endpapers.
Triethylsilane can also facilitate the high yielding reductive formation of dialkyl ethers from carbonyls and silyl ethers. For example, the combination of 4-bromobenzaldehyde, trimethylsilyl protected benzyl alcohol, and Et<sub>3</sub>SiH in the presence of catalytic amounts of FeCl<sub>3</sub> will result in the reduction and benzylation of the carbonyl group (eq 32).<sup>82</sup> Similarly, Cu(OTf)<sub>2</sub> has been shown to aid Et<sub>3</sub>SiH in the reductive etherification of variety of carbonyl compounds with n-octyl trimethylsilyl ether to give the alkyl ethers in moderate to good yields.<sup>83</sup> Likewise, TMSOTf catalyzes the conversion of tetrahydropyranyl ethers to benzyl ethers with Et<sub>3</sub>SiH and benzaldehyde, and diphenylmethyl ethers with Et<sub>3</sub>SiH and diphenylmethyl formate.<sup>84</sup> Symmetrical and unsymmetrical ethers are afforded in good yield from carbonyl compounds with silyl ethers (or alcohols) and Et<sub>3</sub>SiH catalyzed by bismuth trihalide salts.<sup>85</sup> An intramolecular version of this procedure has been nicely applied to the construction of cis-2,6-di- and trisubstituted tetrahydropyrans.<sup>86</sup>

In a related process, triethylsilane plus SnCl<sub>4</sub> can expediently convert aprotically protected aldol products to fully protected 1,3-diols. Moreover, the synthesis of syn-1,3-ethylenedioacetals from 1-(2-methoxyethoxy)ethyl-protected β-hydroxy ketones with SnCl<sub>4</sub> and Et<sub>3</sub>SiH can occur with very high levels of diastereoccontrol (eq 33).<sup>87</sup>

**Ether Cleavages.** Triethylsilane and B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> can also be used for the general cleavage of ether bonds to their corresponding triethylsilyl ether and hydrocarbons.<sup>88</sup> This chemistry can selectively cleave differently substituted ethers (e.g., primary alkyl ethers cleave preferentially over secondary, tertiary, or aryl ether groups), but it should be noted that only a limited number of such examples have been reported. Furthermore, chemoselectivity can be an issue as Et<sub>3</sub>SiH/B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> can deoxygenate primary alcohols and acetals, as well as perform the aforementioned silane alcohols. Nonetheless, Et<sub>3</sub>SiH and TFA are well suited for taking triphenylmethyl (Tril, Tr) protective groups off hydroxyls (eq 34),<sup>73</sup> aziridines,<sup>88</sup> or peptides,<sup>89</sup> even when other acid-sensitive functional groups are present. Triethylsilane has also been employed in the deprotection of triphenylmethyl-protected nucleotides, but with dichloroacetic acid in dichloromethane.<sup>90</sup>

**Ester Reductions and Miscellaneous Reductive Substitutions.** Triethylsilane can react with esters in a number of ways. Aliphatic esters and lactones are reduced to acyclic and cyclic ethers when treated with TiCl<sub>4</sub>, TMSOTf, and Et<sub>3</sub>SiH (eq 35).<sup>91</sup> Propargylic acetates, on the other hand, will undergo reductive cleavage of their C–O bonds when treated with catalytic amounts of indium(III) bromide and Et<sub>3</sub>SiH.<sup>92</sup> Aryl and enol triflates are reduced when exposed to Et<sub>3</sub>SiH and a Pd–phosphine complex (eq 36), whereas aromatic and aliphatic iodoethanes, bromides, and chlorides are dehalogenated with Et<sub>3</sub>SiH and catalytic PdCl<sub>2</sub> (also see eq 11).<sup>93</sup> Curiously, Et<sub>3</sub>SiH and PdCl<sub>2</sub> can also be used to make C–X bonds, as alcohols are converted to the corresponding halide with PdCl<sub>2</sub>, Et<sub>3</sub>SiH, and iodomethane, dibromomethane, or hexachloroethane (eq 37).<sup>94</sup> Likewise, lactones will undergo a ring-opening halosilylation with PdCl<sub>2</sub>, Et<sub>3</sub>SiH, and iodomethane, or allyl bromide, producing the triethylsilyl o-ido- or o-bromoalkanotes.<sup>95</sup>

**Reductive Couplings and Cyclizations.** As previously discussed, triethylsilane can react with both activated (eq 5)<sup>15,16</sup> and non-activated olefins (eq 12).<sup>28</sup> Recent developments in this area include the saturation of alkenes by Et<sub>3</sub>SiH under catalysis by Grubb’s 1st generation catalyst. A particularly elegant application of this chemistry is possible when ring closing metathesis (RCM) is kinetically favored. In such cases one can effect a one-pot ring closure/alkene reduction in good overall yield (eq 38).<sup>96</sup>
Alkenes, along with alkynes, allenes, or dienes, can also participate in triethylsilane promoted reductive couplings. Aldehydes, in particular, are good at coupling with the intermediates of nickel-catalyzed additions of Et₃SiH across alkenes, allenes, dienes, or alkynes (eq 39). These reactions tend to be highly regioselective; as are the indium(III) bromide catalyzed reductive syn aldol between aldehydes, enones, and Et₃SiH (eq 40). Finally, in the presence of ethylaluminum sesquichloride and Et₃SiH, alkylchloroformates participate in what have been termed Friedel–Crafts alkylations of alkenes.

\[
\text{PhCHO} + \text{Me} = \text{C}_2\text{H}_4\xrightarrow{\text{Ni}} \text{Et}_3\text{SiH} \quad (84\%)
\]

\[
\text{CHO} + \text{Et} \longrightarrow \text{C}_2\text{H}_4 \xrightarrow{\text{InBr}_3} \text{Et}_3\text{SiH} \quad (61\%)
\]

Imines can serve as electrophiles in similar processes. For example, tetrahydropyran or tetrahydrofuran containing amino acids are synthesized in good yield from a TiCl₄ catalyzed coupling of cyclic enol ethers, N-tosyl imino ester, and triethylsilane (eq 41).

\[
\text{CHO} + \text{Et} \longrightarrow \text{C}_2\text{H}_4 \xrightarrow{\text{Ni}} \text{Et}_3\text{SiH} \quad (60-98\%)
\]

The combination of Et₃SiH, rhodium, carbon monoxide, and allenyl–carbonyl compounds yields cis-2-triethylsilylvinylcyclopentanols and cyclohexanols (eq 44). This reaction produces hydroxylations with Et₃SiH, where no particular advantage is either attributed or demonstrated for Et₃SiH over other silanes. Finally, reductive Nazarov cyclizations can also take place with Et₃SiH and a Lewis acid.

When reacting alkenes with triethylsilane it is necessary to keep in mind that the PdCl₂/Et₃SiH combination also promotes the double bond isomerization of mono substitutated aliphatic olefins, and \(\alpha\)-alkylidene cyclic carbonyl compounds are isomerized to \(\alpha,\beta\)-unsaturated cyclic carbonyls with tris(triphenylphosphine) rhodium chloride.

**Aromatic Silylations.** Aryltriethylsilanes are synthesized in moderate to good yield from electron-rich meta- and para-substituted aryl iodides, by Pd(P-tBu)₃ in the presence of K₂PO₄ and triethylsilane. Platinum oxide in conjunction with sodium acetate and Et₃SiH silylates meta and para substituted aryl iodides and bromides that contain electron-withdrawing groups. ortho-Triethylsilyl aromatics are accessed with Ru₃(CO)₁₂ using azoles, imines, pyridines, amides, and esters as directing groups; the system tolerates electron-donating and withdrawing groups (eq 45).

**Generation of Other Triethylsilyl Reagents, etc.** Triethylsilane is also used in the synthesis of various other reagents for organic synthesis. Triethylsilyl cyanide, which is used for the silylcyanation of aldehydes and ketones, can be prepared from...
Et₃SiH and acetonitrile in the presence of catalytic amounts of 
Cp(CO)₂FeMe.¹⁶ Bromotriethylsilane is prepared when Et₃SiH 
reacts with copper(II) bromide and catalytic amounts of copper(I) 
ioide¹⁴⁷ or with PdCl₂ and allyl bromide.¹¹⁵ Et₃SiH can also 
reduce Bu₃SnCl to Bu₃SnH, which when carried out in the presence 
of alkynes, allenes, or alkenes can undergo Lewis acid promoted 
hydrostilbination reactions (eq 46).¹¹⁹ This represents the first 
example of Lewis acid catalyzed hydrostilbations with in situ 
generated tributylstilbene hydride. Significantly, Et₃SiH succeeded in 
this reaction where hydrosiloxanes failed. Lastly, Et₃SiH reacts 
with indium(III) chloride to generate dichloroindium hydride.¹¹⁹

\[
R \quad R^1 \quad R^2
\]

\[
\text{toluene, } 0 \degree C \text{ to } \text{m (70-90%)}
\]

\[
Z.E \text{ } \approx 90:10
\]

(46)

**Related Reagents.** Phenylsilane–Cesium Fluoride; Tri-n-butylstannane; Tricarboxylchlororidium–Diethyl(methyl) Silane–Carbon Monoxide; Triethylsilane–Trifluoroacetic Acid.


A list of General Abbreviations appears on the front Endpapers.

Avoid Skin Contact with All Reagents