

Triethylsilane¹[617-86-7] C₆H₁₆Si (MW 116.31)

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

InChIKey = AQRLNPVMDITEJU-UHFFFAOYAL

(mild reducing agent for many functional groups)

Physical Data: mp -156.9 °C; bp 107.7 °C; *d* 0.7309 g cm⁻³.**Solubility:** insol H₂O; 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.

Original Commentary

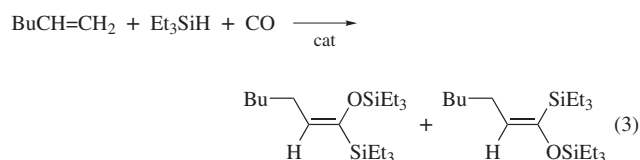
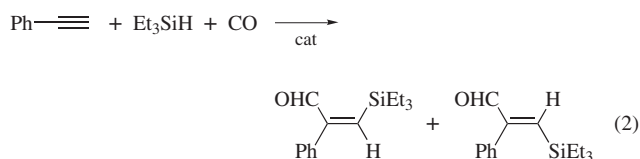
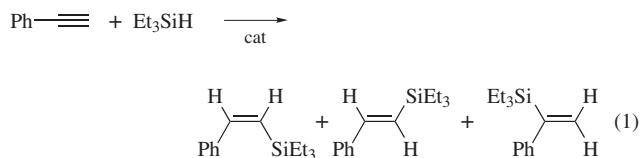
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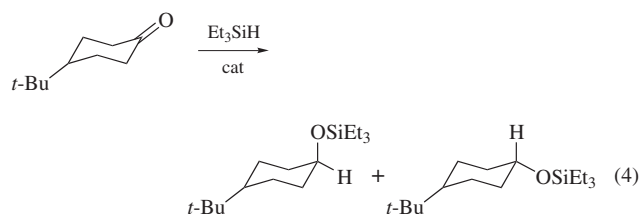
Introduction. Triethylsilane serves as an exemplar for organosilicon hydride behavior as a mild reducing agent. It is frequently chosen as a synthetic reagent because of its availability, convenient physical properties, and economy relative to other organosilicon hydrides which might otherwise be suitable 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 alkynes undergo hydrosilylations easily with triethylsilane in the presence of platinum,³ rhodium,^{3a,4} ruthenium,⁵ osmium,⁶ or iridium⁴ catalysts. For example, phenylacetylene can form three possible isomeric hydrosilylation products with triethylsilane; the (*Z*)- β -, the (*E*)- β -, and the α -products (eq 1). The (*Z*)- β -isomer is formed exclusively or preferentially with ruthenium⁵ and some rhodium⁴ catalysts, whereas the (*E*)- β -isomer is the major product formed with platinum³ or iridium⁴ catalysts. In the presence of a catalyst and carbon monoxide, terminal alkynes undergo silylcarbonylation reactions with triethylsilane to give (*Z*)- and (*E*)- β -silylacrylaldehydes.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 °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)₃]_{*n*}) reacts under

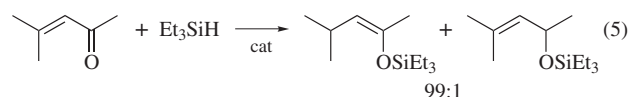
50 atm of carbon monoxide to give a 50% yield of a mixture of the (*Z*)- and (*E*)-enol silyl ether isomers in a 1:2 ratio (eq 3).⁹ Hydrolysis yields the derived acylsilane quantitatively.⁹



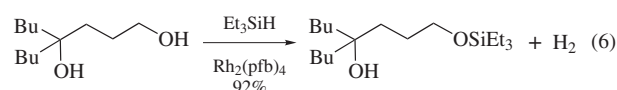
A number of metal complexes catalyze the hydrosilylation of various carbonyl compounds by triethylsilane.¹⁰ Stereoselectivity is observed in the hydrosilylation of ketones¹¹ as in the reactions of 4-*t*-butylcyclohexanone and triethylsilane catalyzed by ruthenium,¹² chromium,¹³ and rhodium^{12,14} metal complexes (eq 4). Triethylsilane and **Chlorotris(triphenylphosphine)rhodium(I)** catalyst effect the regioselective 1,4-hydrosilylation of α,β -unsaturated ketones and aldehydes.^{15,16} Reduction of mesityl oxide in this manner results in a 95% yield of product that consists of 1,4- and 1,2-hydrosilylation isomers in a 99:1 ratio (eq 5). This is an exact complement to the use of phenylsilane, where the ratio of respective isomers is reversed to 1:99.¹⁶



(Ph ₃ P) ₃ RuCl ₂ , AgTFA, PhMe, Δ	5:95
Et ₄ N ⁺ [HCf ₂ (CO) ₁₀] ⁻ , DME, Δ	10:90
(Ph ₃ P) ₃ RhCl, PhMe, Δ	11:89
[Rh(η^3 -C ₃ H ₅){P(OMe) ₃] ₃ , PhH	29:71

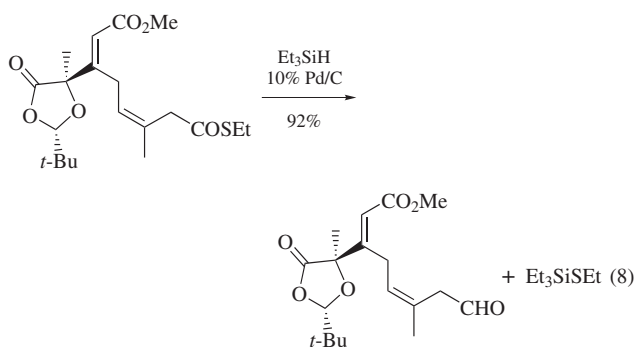
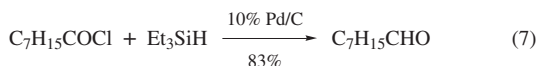


Silane Alcoholysis. Triethylsilane reacts with alcohols in the presence of metal catalysts to give triethylsilyl ethers.¹⁷ The use of dirhodium(II) perfluorobutyrate as a catalyst enables regioselective formation of monosilyl ethers from diols (eq 6).^{17a}



Formation of Singlet Oxygen. Triethylsilane reacts with ozone at $-78\text{ }^{\circ}\text{C}$ in inert solvents to form triethylsilyl hydrotrioxide, which decomposes at slightly elevated temperatures to produce triethylsilanol and *Singlet Oxygen*. This is a convenient way to generate this species for use in organic synthesis.¹⁸

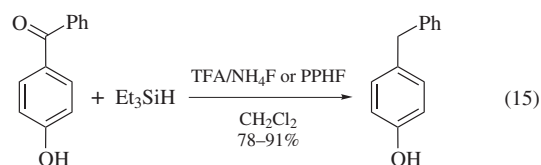
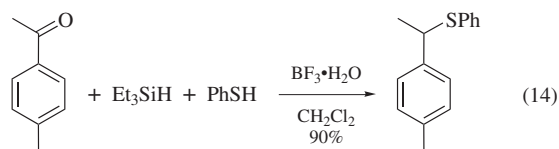
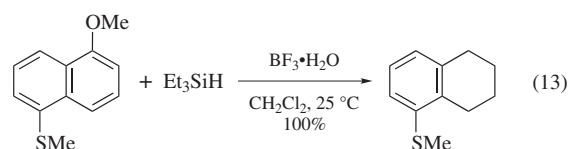
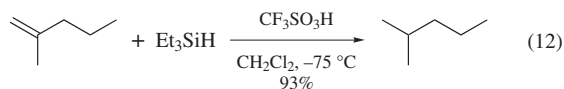
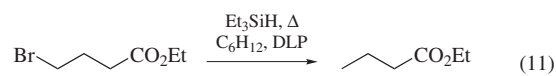
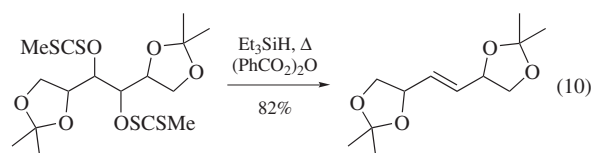
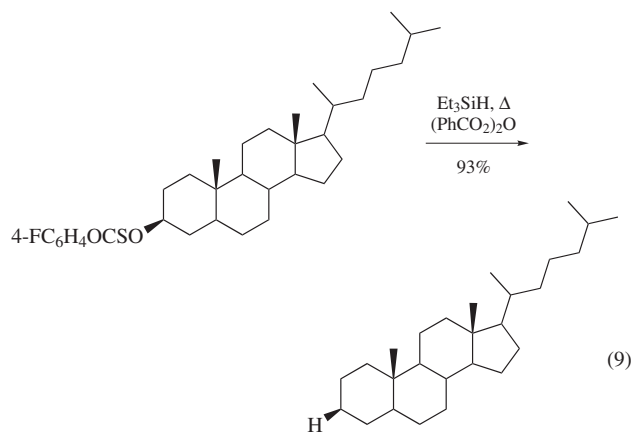
Reduction of Acyl Derivatives to Aldehydes. Aryl chlorides and bromides give modest yields of aryl aldehydes when refluxed in diethyl ether with triethylsilane and *Aluminum Chloride*.¹⁹ Better yields of both alkyl and aryl aldehydes are obtained from mixtures of acyl chlorides or bromides and triethylsilane 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

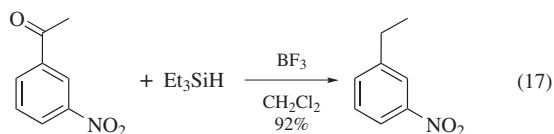
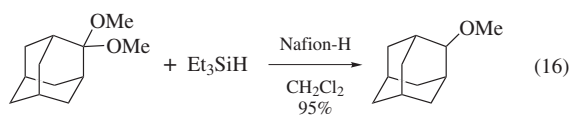


Radical Chain Reductions. Triethylsilane can replace toxic and difficult to remove organotin reagents for synthetic reductions under radical chain conditions. Although it is not as reactive as *Tributylstannane*,²² careful choice of initiator, solvent, and additives leads to effective reductions of alkyl 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-3 β -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).²³

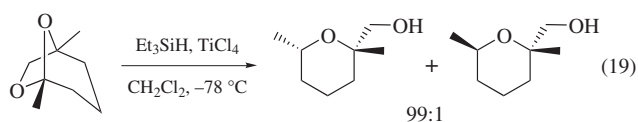
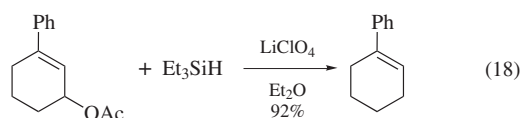
Ionic Hydrogenations and Reductive Substitutions. The polar nature of the Si-H bond enables triethylsilane to act as a hydride donor to electron-deficient centers. Combined with Brønsted or Lewis acids this forms the basis for many useful synthetic transformations.²⁷ Use of *Trifluoromethanesulfonic Acid* (triflic acid) at low temperatures enables even simple alkenes to be reduced to alkanes in high yields (eq 12).²⁸ *Boron Trifluoride* monohydrate is effective in promoting the reduction of polycyclic aromatic compounds (eq 13).²⁹ Combined with thiols,

it enables sulfides to be prepared directly from aldehydes and ketones (eq 14).³⁰ Combinations of triethylsilane with either *Trifluoroacetic Acid*/ammonium fluoride or *Pyridinium Poly(hydrogen fluoride)* (PPHF) are effective for the reductions of alkenes, alcohols, and ketones (eq 15).³¹ Immobilized strong acids such as iron- or copper-exchanged *Montmorillonite K10*³² or the superacid *Nafion-H*³³ facilitate reductions of aldehydes and ketones³² or of acetals³³ by increasing the ease of product separation (eq 16). Boron trifluoride and triethylsilane are an effective combination for the reduction of alcohols, aldehydes, ketones (eq 17),³⁴ and epoxides.³⁵ *Boron Trifluoride Etherate* sometimes may be substituted for the free gas.³⁶





Triethylsilane in 3M ethereal **Lithium Perchlorate** solution effects the reduction of secondary allylic alcohols and acetates (eq 18).³⁷ The combination of triethylsilane and **Titanium(IV) Chloride** is a particularly effective reagent pair for the selective reduction of acetals.³⁸ Treatment of (\pm)-frontalin with this pair gives an 82% yield of tetrahydropyran products with a *cis:trans* ratio of 99:1 (eq 19).^{38b} This exactly complements the 1:99 product ratio of the same products obtained with **Diisobutylaluminum Hydride**.^{38b}



Triethylsilane and trityl salts.³⁹ or **Trimethylsilyl Trifluoromethanesulfonate**⁴⁰ are effective for the reduction of various ketones and acetals, as are combinations of **Chlorotrimethylsilane** and indium(III) chloride⁴¹ and **Tin(II) Bromide** and **Acetyl Bromide**.⁴² Isophthalaldehyde undergoes reductive polycondensation to a polyether when treated with triethylsilane and **Triphenylmethyl Perchlorate**.⁴³

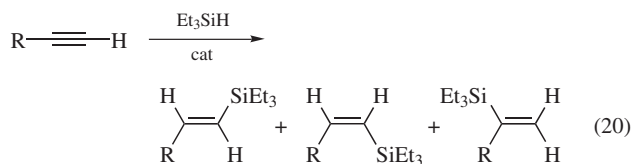
Triethylsilane reduces nitrilium ions to aldimines,⁴⁴ diazonium ions to hydrocarbons,⁴⁵ and aids in the deprotection of amino acids.⁴⁶ With aluminum halides, it reduces alkyl halides to hydrocarbons.⁴⁷

First Update

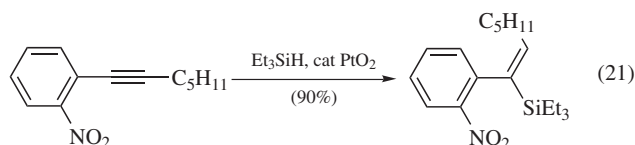
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Additional Hydrosilylations. Hydrosilylations of terminal alkynes with triethylsilane (eq 1) have been improved in terms of their regio- and stereocontrol as well as in other aspects of their operation. Through the employment of Pt(DVDS),⁴⁸ Pt-catalyzed hydrosilylations of 1-alkynes³ 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 hydrosilylation of aryl alkynes under *ortho*-substituent regiocontrol (eq 21).⁴⁹ Strong preference for the (*E*)- β -vinylsilanes during the hydrosilylation of 1-alkynes has

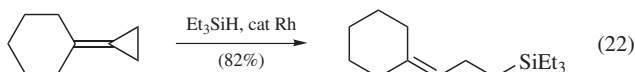
also been observed with cationic Ru-catalysts⁵⁰ and [RhCl(nbd)]₂/dppp,⁵¹ the latter of which can also be employed in water (eq 20). Hydrosilylations afford α -vinylsilanes when catalyzed by [CpRu(MeCN)₃]PF₆⁵² (eq 20). (*Z*)- β -Vinylsilanes are similarly made under [RuCl₂(*p*-cymene)]₂ catalysis⁵³ or by the *trans* hydrosilylation of 1-alkynes under Lewis acid (AlCl₃)⁵⁴ catalysis.



R = C ₁₀ H ₂₁	[RhCl(nbd)] ₂ + dppp	93:3:4
R = Ph	[Cp*Rh(BINAP)](SbF ₆) ₂	97:0:3
R = C ₄ H ₉	Pt(DVDS)EP	100:0:0
R = C ₄ H ₉	[RuCl ₂ (<i>p</i> -cymene)] ₂	4:96:0
R = PhCH ₂	AlCl ₃	0:100:0
R = C ₆ H ₁₂ CO ₂ H	[CpRu(MeCN) ₃]PF ₆	2.5:2.5:95



AlCl₃ can also promote the hydrosilylation of allenes and alkenes.⁵⁴ With regard to the hydrosilylation of alkenes; Rh-catalyzed reactions of Et₃SiH and methylenecyclopropanes provide a convenient route to homoallylic silanes (eq 22).⁵⁵

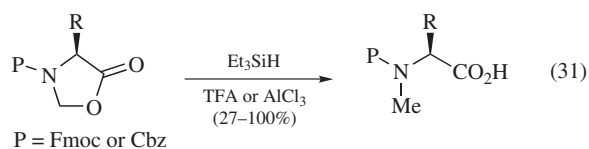


The hydrosilylation of carbonyl compounds with Et₃SiH (eq 4) has also been the subject of additional research. Owing to these efforts, carbonyls can now be directly converted to their triethylsilyl (TES) ethers with copper catalysts in the company of a bidentate phosphine⁵⁶ or *N*-heterocyclic carbene⁵⁷ ligand. Triethylsilyl ethers can also be made from carbonyl compounds and Et₃SiH in the presence of rhenium(V) oxo-complexes.⁵⁸

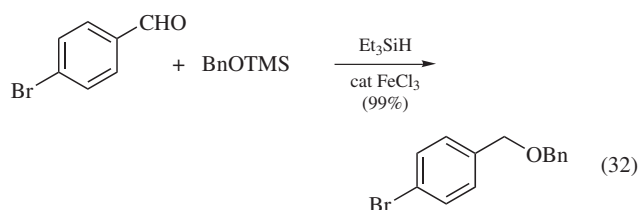
Additional Silane Alcoholysis. The direct silylation of alcohols with triethylsilane (eq 26)¹⁷ continues to be an interesting, if somewhat underused, method to TES protect alcohols. Recent works have demonstrated that this process is promoted by a number of catalysts including PdCl₂,⁵⁹ a Au(I) catalyst,⁶⁰ and the Lewis acid B(C₆F₆)₃⁶¹ (eq 23).



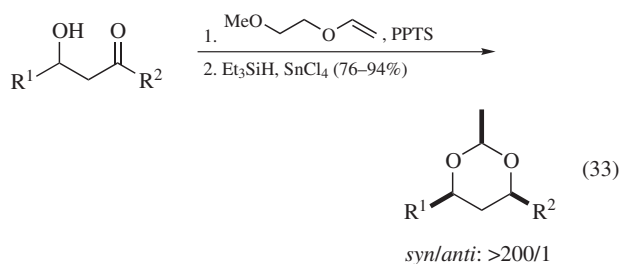
R =	Catalyst	% Yield
1 and 2 aliphatic	PdCl ₂	78–98
1, 2, 3 aliphatic or Ar	Au(I)	80–100
2, 3 aliphatic or Ar	B(C ₆ F ₆) ₃	95–100



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 Et₃SiH in the presence of catalytic amounts of FeCl₃ will result in the reduction and benzylation of the carbonyl group (eq 32).⁸² Similarly, Cu(OTf)₂ has been shown to aid Et₃SiH in the reductive etherification of variety of carbonyl compounds with *n*-octyl trimethylsilyl ether to give the alkyl ethers in moderate to good yields.⁸³ Likewise, TMSOTf catalyzes the conversion of tetrahydropyranyl ethers to benzyl ethers with Et₃SiH and benzaldehyde, and diphenylmethyl ethers with Et₃SiH and diphenylmethyl formate.⁸⁴ Symmetrical and unsymmetrical ethers are afforded in good yield from carbonyl compounds with silyl ethers (or alcohols) and Et₃SiH catalyzed by bismuth trihalide salts.⁸⁵ An intramolecular version of this procedure has been nicely applied to the construction of *cis*-2,6-di- and trisubstituted tetrahydropyrans.⁸⁶

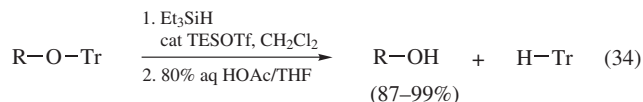


In a related process, triethylsilane plus SnCl₄ can expediently convert appropriately protected aldol products to fully protected 1,3-diols. Moreover, the synthesis of *syn*-1,3-ethylidene acetals from 1-(2-methoxyethoxy)ethyl-protected β-hydroxy ketones with SnCl₄ and Et₃SiH can occur with very high levels of diastereocontrol (eq 33).⁸⁷



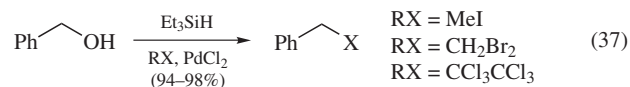
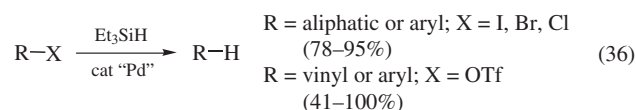
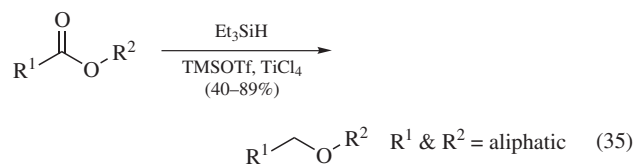
Ether Cleavages. Triethylsilane and B(C₆F₅)₃ can also be used for the general cleavage of ether bonds to their corresponding triethylsilyl ether and hydrocarbon.^{61b} This chemistry can selectively cleave differently substituted ethers (e.g., primary alkyl ethers cleave preferentially over secondary, 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 Et₃SiH/B(C₆F₅)₃ can deoxygenate primary alcohols and acetals, as well as perform the aforementioned silane alcoholyses. Nonetheless, Et₃SiH and TFA are well suited for taking triphenylmethyl (trityl, Tr) protective groups off hydroxyls (eq 34),⁷³ aziridines,⁸⁸ or peptides⁸⁹ even when other acid-sensitive func-

tional groups are present. Triethylsilane has also been employed in the deprotection of triphenylmethyl-protected nucleotides, but with dichloroacetic acid in dichloromethane.⁹⁰

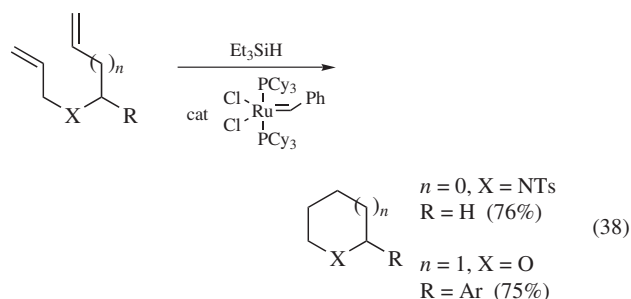


Ester Reductions and Miscellaneous Reductive Substitutions.

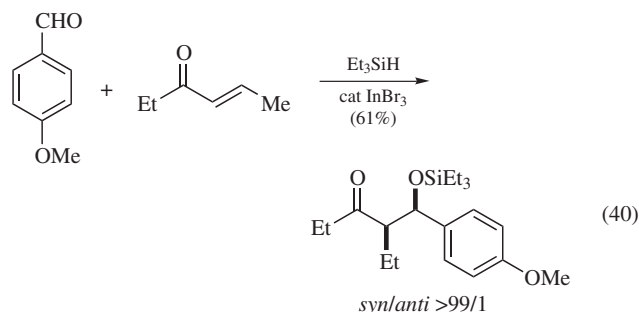
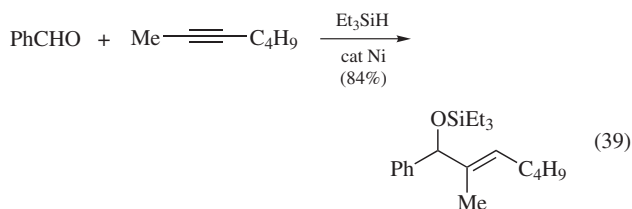
Triethylsilane can react with esters in a number of ways. Aliphatic esters and lactones are reduced to acyclic and cyclic ethers when treated with TiCl₄, TMSOTf, and Et₃SiH (eq 35).⁹¹ Propargylic acetates, on the other hand, will undergo reductive cleavage of their C–O bonds when treated with catalytic amounts of indium(III) bromide and Et₃SiH.⁹² Aryl and enol triflates are reduced when exposed to Et₃SiH and a Pd–phosphine complex⁹³ (eq 36), whereas aromatic and aliphatic iodides, bromides, and chlorides are dehalogenated with Et₃SiH and catalytic PdCl₂ (also see eq 11²³). Curiously, Et₃SiH and PdCl₂ can also be used to make C–X bonds, as alcohols are converted to the corresponding halide with PdCl₂, Et₃SiH, and iodomethane, dibromomethane, or hexachloroethane (eq 37).⁹⁴ Likewise, lactones will undergo a ring-opening halosilylation with PdCl₂, Et₃SiH, and iodomethane, or allyl bromide, producing the triethylsilyl ω-iodo- or ω-bromoalkanoates.⁹⁵



Reductive Couplings and Cyclizations. As previously discussed, triethylsilane can react with both activated (eq 5)^{15,16} and non-activated olefins (eq 12²⁸). Recent developments in this area include the saturation of alkenes by Et₃SiH 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).⁹⁶

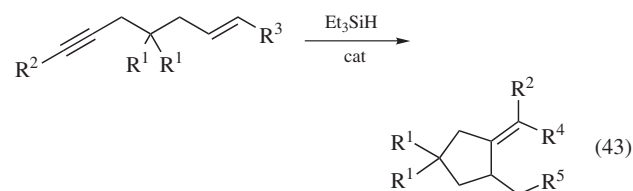
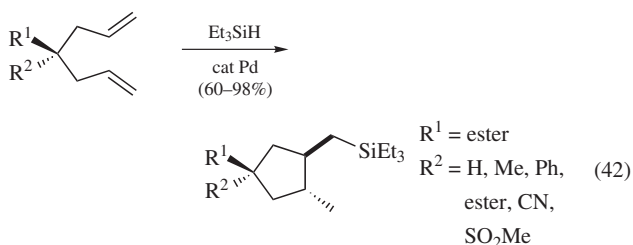
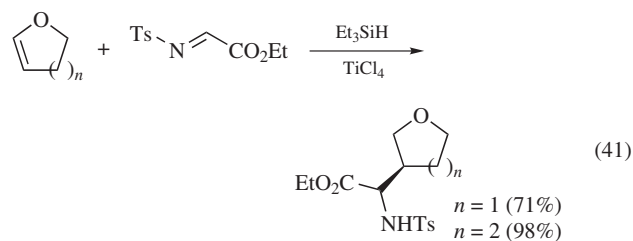


Alkenes, along with alkynes, allenes, or dienes, can also participate in triethylsilane promoted reductive couplings. Aldehydes, in particular, are good at coupling with the intermediates of nickel-catalyzed additions of Et_3SiH across alkenes, allenes, dienes, or alkynes (eq 39).⁹⁷ These reactions tend to be highly regioselective; as are the indium(III) bromide catalyzed reductive syn aldol between aldehydes, enones, and Et_3SiH (eq 40).⁹⁸ Finally, in the presence of ethylaluminum sesquichloride and Et_3SiH , alkylchloroformates participate in what have been termed Friedel–Crafts alkylations of alkenes.⁹⁹

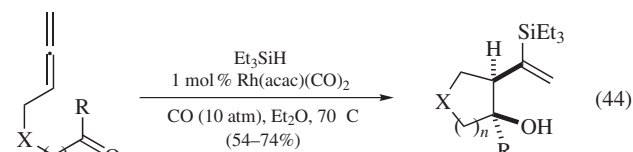


Imines can serve as electrophiles in similar processes. For example, tetrahydropyran or tetrahydrofuran containing amino acids are synthesized in good yield from a TiCl_4 catalyzed coupling of cyclic enol ethers, *N*-tosyl imino ester, and triethylsilane (eq 41).¹⁰⁰ Triethylsilane and a palladium-catalyst can prompt the cyclization–hydrosilylation of 1,6- and 1,7-dienes with good yields and moderate to high stereoselectivity (eq 42).¹⁰¹ Cationic rhodium catalyzes a cyclization–hydrosilylation of 1,6-enynes,¹⁰² whereas palladium catalyzes a regio- and stereoselective cycloreduction.¹⁰³ This reaction has also been applied to haloenynes¹⁰⁴ and bimetallic cobalt/rhodium nanoparticles in an atmosphere of carbon monoxide to effect a carbonylative silylcarbocyclization (eq 43).¹⁰⁵ 1,6-Diynes with cationic platinum, or cationic rhodium, in conjunction with Et_3SiH undergo a cyclization–hydrosilylation.^{106,107} The combination of Et_3SiH , rhodium, carbon monoxide, and allenyl–carbonyl compounds yields *cis*-2-triethylsilylvinylcyclopentanol and cyclohexanol (eq 44).¹⁰⁸ For this reaction the investigators mention that Et_3SiH is superior to Ph_3SiH , Me_2PhSiH , and $(\text{EtO})_3\text{SiH}$. This contrasts most other reports of hydrosilylations with Et_3SiH , where no particular advantage is either attributed or demonstrated for Et_3SiH over other silanes. Finally, reductive Nazarov cyclizations can also take place with Et_3SiH and a Lewis acid.¹⁰⁹

When reacting alkenes with triethylsilane it is necessary to keep in mind that the $\text{PdCl}_2/\text{Et}_3\text{SiH}$ combination also promotes the double bond isomerization of monosubstituted aliphatic olefins¹¹⁰ and α,β -unsaturated cyclic carbonyl compounds are isomerized to α,β -unsaturated cyclic carbonyls with tris(triphenylphosphine) rhodium chloride.¹¹¹

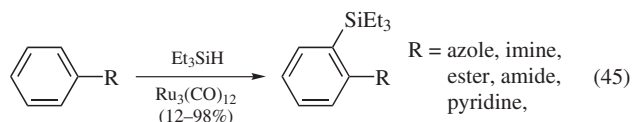


R^1	R^2	R^3	Catalyst	R^4	R^5	% Yield
CO_2Et	H	Ph	$\text{Pd}(\text{dpe})\text{Cl}_2$	H	Ph	85
Me	Me	H	$[\text{Rh}(\text{COD})_2]\text{SbF}_6$	SiEt_3	H	65
CO_2Me	H	H	$\text{Co}_2\text{Rh}_2 + \text{CO}$	SiEt_3	CHO	93



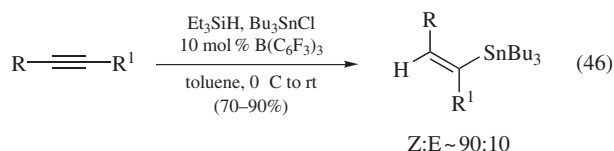
$\text{X} = \text{C}(\text{CO}_2\text{Et})_2, \text{NTs, O}; \text{R} = \text{H, Me, Et}; n = 1, 2$

Aromatic Silylations. Aryltriethylsilanes are synthesized in moderate to good yield from electron-rich *meta*- and *para*-substituted aryl iodides, by $\text{Pd}(\text{P-}t\text{Bu})_3$ in the presence of K_3PO_4 and triethylsilane.¹¹² Platinum oxide in conjunction with sodium acetate and Et_3SiH silylates *meta* and *para* substituted aryl iodides and bromides that contain electron-withdrawing groups.¹¹³ *ortho*-Triethylsilyl aromatics are accessed with $\text{Ru}_3(\text{CO})_{12}$ using azoles, imines, pyridines, amides, and esters as directing groups; the system tolerates electron-donating and withdrawing groups (eq 45).¹¹⁴ This method has also been applied to the silylation of benzylic C–H bonds.¹¹⁵



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

Et_3SiH and acetonitrile in the presence of catalytic amounts of $\text{Cp}(\text{CO})_2\text{FeMe}$.¹¹⁶ Bromotriethylsilane is prepared when Et_3SiH reacts with copper(II) bromide and catalytic amounts of copper(I) iodide¹¹⁷ or with PdCl_2 and allyl bromide.¹¹⁸ Et_3SiH can also reduce Bu_3SnCl to Bu_3SnH , which when carried out in the presence of alkynes, allenes, or alkenes can undergo Lewis acid promoted hydrostannation reactions (eq 46).¹¹⁹ This represents the first example of Lewis acid catalyzed hydrostannations with in situ generated tributyltin hydride. Significantly, Et_3SiH succeeded in this reaction where hydrosiloxanes failed. Lastly, Et_3SiH reacts with indium(III) chloride to generate dichloroindium hydride.¹¹⁹



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

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