Triethoxysilane

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Introduction

Triethoxysilane (TES) is an important chemical reagent in the synthesis of various organosilicon compounds. It is a colourless transparent liquid (bp 134–135 °C) with a characteristic ether odour. Triethoxysilane is an organosilane and has been widely used in organic synthesis as a mild reducing agent. It has been used for asymmetric hydrosilylation of ketones in order to obtain the corresponding alcohols.1 Additionally, (EtO)3SiH is applied as silylation reagent in regio- and stereoselective hydrosilylations.2 It is able to cleave a C–C bond of the four-membered ring of biphenylene forming the corresponding 2-silylbiphenyls.3 TES is also used in reductive etherification of aldehydes in the presence of the catalyst system InCl3/TMSCl.4

Triethoxysilane is commercially available but it can also easily be synthesized in the reaction of trichlorosilane with anhydrous ethyl alcohol (Scheme 1).5

\[
\text{HSiCl}_3 + 3\text{EtOH} \rightarrow \text{HSi(OEt)}_3 + 3\text{HCl}
\]

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Use of Triethoxysilane</th>
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<tbody>
<tr>
<td>(A)</td>
<td>Beller and co-workers described a procedure for efficient reduction of tertiary amides. The reaction was carried out in the presence of inexpensive zinc catalyst with (EtO)3SiH under mild conditions. Diverse functional groups present in the molecule (ester, ether, nitro, cyano, azo) are tolerated. The desired products were isolated in good to high yields.</td>
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<td>(B)</td>
<td>An efficient rhodium(I)-catalyzed reaction between arenediazonium tosylate salts and triethoxysilane led to aryltriethoxysilanes in good to high yields. The synthesis was carried out in the presence of Bu4NI and Et3N.</td>
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<td>(C)</td>
<td>The preparation of various nitriles from primary carboxylic amides can be realized by iron-catalyzed [Et3NH, HFe3(CO)11] dehydrogenation with triethoxysilane as dehydrating agents. The experiment was carried out using toluene as a solvent in 100 °C.</td>
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<td>(D)</td>
<td>Ritter and co-workers reported a selective 1,2-hydrosilylation of conjugated dienes using triethoxysilane in the presence of catalytic amounts of platinum precatalyst. The catalyst was activated with methylmagnesium chloride (MeMgCl) at –45 °C, then (EtO)3SiH and diene were added. The mixture was heated to 50 °C. The product was formed with high selectivity.</td>
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\[
\begin{align*}
\text{O} & \quad \text{N} \\
\text{R}^1 & \quad \text{R}^2 & \quad \text{R}^3 \\
\text{N} & \quad \text{Zn(OAc)}_2 (10 \text{ mol\%}) \\
\text{(EtO)}_3\text{SiH} (3 \text{ equiv}), \text{THF} & \quad \text{R}^1 \quad \text{N} \quad \text{R}^2 \quad \text{R}^3 & \quad 73–99\% \text{ yield} \\
\end{align*}
\]

\[
\begin{align*}
\text{N} & \quad \text{Ts}^+ & \quad \text{O}^- \\
\text{R} & \quad \text{N}^+ & \quad \text{Et}_3\text{N}, \text{Bu}_4\text{NI}, \text{DMF} & \quad 1. (\text{Rh(cod)Cl})_2, \text{Et}_3\text{N} \quad \text{Si(OEt)}_3 \\
\quad & \quad \text{R} & \quad \text{Et}_3\text{SiH}, \text{reflux}, 8 \text{ h} & \quad 76–90\% \text{ yield} \\
\end{align*}
\]

\[
\begin{align*}
\text{O} & \quad \text{N} & \quad \text{NH}_2 \\
\text{R} & \quad \text{NH} & \quad \text{(Et}_3\text{NH})_2\text{HFe}_3\text{(CO)}_{11} (2 \text{ mol\%}) \\
\quad & \quad \text{(EtO)}_3\text{SiH}, \text{PhiMe}, 100 \degree \text{C} & \quad 55\% \text{ yield} \\
\end{align*}
\]

\[
\begin{align*}
\varepsilon & \quad + \quad \text{HSi(OEt)}_3 & \quad \text{MeMgCl} (1.0 \text{ mol\%}) \\
\quad & \quad \text{CH}_2\text{Cl}_2 & \quad \text{(EtO)}_3\text{SiH}, \text{PhiMe}, 100 \degree \text{C} & \quad 85\% \text{ yield} \\
\end{align*}
\]

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Organosilanes are convenient reagents in the selective reduction of nitroarenes. The corresponding aniline was formed with (EtO)3SiH in the presence of a catalyst consisting of FeBr2 and Ph3P. The desired product was isolated in good yield (66%).

Riland and co-workers described the stereodivergent synthesis of polysubstituted enynes, which are useful building blocks. Vinyldisiloxanes (Z)-2 and (E)-2 were obtained in high yields with an α/β selectivity of 80:20. These products were then converted into trisubstituted enynes, which were isolated with full retention of the stereochemistry.

The asymmetric silylcyclization of 1,6-enynes with (EtO)3SiH was carried out in the presence of a rhodium catalyst generated in situ. It was observed that these reactions provide optically active silylalkylidene cyclopentane and pyrrolidine derivatives. These products were formed in good yields and with high enantioselectivities.

(EtO)3SiH can be applied as a mild reducing agent for catalytic reductive dehydration of tertiary amide to the corresponding enamine catalyzed by potassium tert-butoxide (t-BuOK). The reaction leading to the enamine proceeded with high conversion ratio.

References


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