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This feature focuses on a reagent chosen by a postgraduate, highlighting the uses and preparation of the reagent in current research.

Allyltrimethylsilane

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Introduction

Allyltrimethylsilane is an important reagent for the synthesis of homoallyl alcohols, ethers, amines, \( \alpha,\beta \)-acetylenic ketones, \( \beta,\gamma \)-unsaturated ketones, etc., which are utilized as important building blocks for the synthesis of biologically active molecules. The allylation of carbonyl compounds is one of the most important C–C bond-forming reactions. The use of allyltrimethylsilane opens a new facet in the allylation reaction. The reaction of an allyltrimethylsilane with a carbonyl compound under Lewis acid conditions or in the presence of fluoride ions, known as the Sakurai–Hosomi reaction\(^1\), has been extensively studied and applied successfully in organic synthesis. In addition to allylation reactions, other reactions such as cyclization\(^2\) or ring-opening reaction\(^3\) are also carried out using the reagent.

Abstracts

(A) Homoallylic alcohols can be synthesized by coupling carbonyl compounds with allyltrimethylsilane.\(^4\) This methodology was extended for the synthesis of verbalactone from hexanal using highly diastereo- and enantioselective allylation and a Yamaguchi macro lactonization.\(^4d\)

\[
\begin{align*}
\text{H}_3\text{C} & \quad \text{O} \\
\text{H} & \quad \text{O} \\
\text{SiMe}_3 & \quad \text{OH} \\
\end{align*}
\]

steps

(B) Various \( \beta,\gamma \)-unsaturated ketones have been synthesized by allylation of acid chlorides with allyltrimethylsilane in the presence of 5 mol% of indium tribromide as catalyst.\(^5\)

\[
\begin{align*}
\text{O} \\
\text{R} \\
\text{Cl} \\
+ \\
\text{SiMe}_3 \\
\text{InBr}_3 (5 \text{ mol}%) \\
\text{CH}_2\text{Cl}_2, \text{r.t., 35–60 min} \\
\end{align*}
\]

(C) Lee et al. reported on the conjugate addition of allylsilane to \( \alpha,\beta \)-unsaturated carbonyl compounds in which a catalytic amount of indium was used in the presence of trimethylsilylchloride as an activator in good yields.\(^6\)

\[
\begin{align*}
\text{O} \\
\text{R} \\
\text{R'} \\
\text{E or Z} \\
(1.1 \text{ equiv}) \\
\text{TMSCl (5 equiv)} \\
\text{CH}_2\text{Cl}_2, \text{r.t., 30 min} \\
\end{align*}
\]

(D) A convenient and highly regioselective method for the preparation of internally arylated allylsilanes by treating allyltrimethylsilane with aryl triflates using palladium acetate as catalyst was reported.\(^7\)

\[
\begin{align*}
\text{O} \\
\text{R} \\
\text{OTf} \\
+ \\
\text{SiMe}_3 \\
Pd(OAc)_2 \\
\text{DPPF} \\
\end{align*}
\]

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(E) Iodine catalyzes efficiently the three-component condensation of aldehydes, benzyl carbamate, and allyltrimethylsilane to afford the corresponding protected homoallylic amines in excellent yields. The same reaction is also catalyzed by bismuth or scandium triflate.

(F) Kiegiel and Jurczak reported the diastereoselective addition of allylic reagents to chiral carbon ketoimides derived from Oppolzer’s sultam leading to the formation of a tertiary stereogenic centre.

(G) Hwu and co-workers developed a sequential process involving alkylation, free-radical cyclization and elimination reaction between carbonyl compounds and allyltrimethylsilane in acetic acid to give silicon-containing cyclopentanes with anexo-methylene unit in 52–71% yields.

(H) Lewis acid catalyzed condensation of carbonyl derivatives (ketones, aldehydes, ketals, hemiketals, orthoesters, ortholactones) with allylic silanes and alcohols (or silyl ethers) produces homoallylic ethers in a highly diastereoselective manner.

(I) A mild method for the chemoselective alkylation of acetals has been developed using catalytic amounts of TMS triflate (5–20 mol%) in ionic liquids as solvents. The same reaction can also be carried out by using FeCl₃ as catalyst.

References

(2) Jervis, P. J.; Kariuki, B. M.; Cox, L. R. Org. Lett. 2006, 8, 4649.