

SYNLETT Spotlight 249

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

Allyltrimethylsilane

Compiled by Pabitra Kumar Kalita

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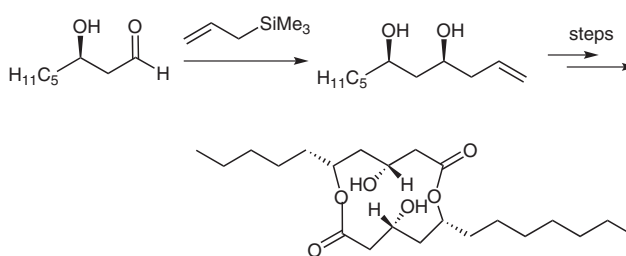
Introduction

Allyltrimethylsilane is an important reagent for the synthesis of homoallyl alcohols, ethers, amines, α,β -acetylenic ketones, β,γ -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

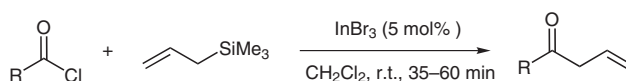
facet in the allylation reaction. The reaction of an allyltrimethylsilane with a carbonyl compound under Lewis acid conditions or in the presence of fluoride ions, known as the Sakurai–Hosomi reaction¹ has been extensively studied and applied successfully in organic synthesis. In addition to allylation reactions, other reactions such as cyclization² or ring-opening reaction³ are also carried out using the reagent.

Abstracts

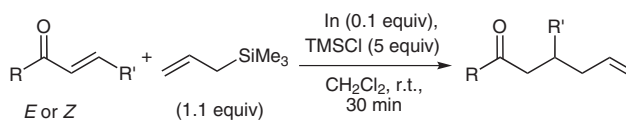
(A) Homoallylic alcohols can be synthesized by coupling carbonyl compounds with allyltrimethylsilane.⁴ This methodology was extended for the synthesis of verbalactone from hexanal using highly diastereo- and enantioselective allylation and a Yamaguchi macro-lactonization.^{4d}



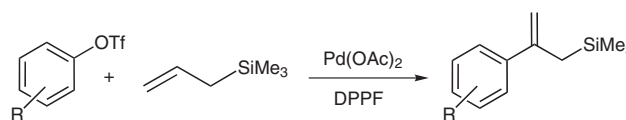
(B) Various β,γ -unsaturated ketones have been synthesized by allylation of acid chlorides with allyltrimethylsilane in the presence of 5 mol% of indium tribromide as catalyst.⁵



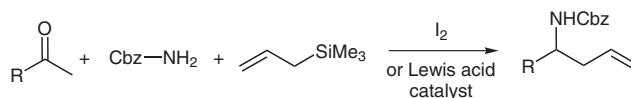
(C) Lee et al. reported on the conjugate addition of allylsilane to α,β -unsaturated carbonyl compounds in which a catalytic amount of indium was used in the presence of trimethylsilylchloride as an activator in good yields.⁶



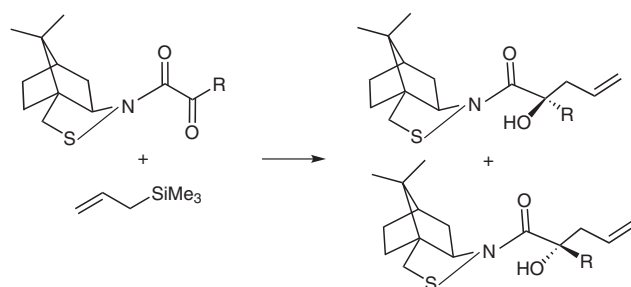
(D) A convenient and highly regioselective method for the preparation of internally arylated allylsilanes by treating allyltrimethylsilane with aryl triflates using palladium acetate as catalyst was reported.⁷



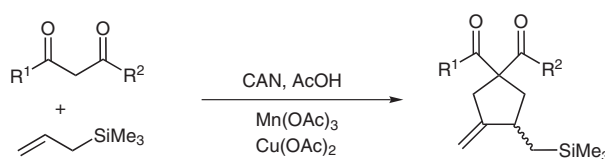
(E) Iodine catalyzes efficiently the three-component condensation of aldehydes, benzyl carbamate, and allyltrimethylsilane to afford the corresponding protected homoallylic amines in excellent yields.^{8a} The same reaction is also catalyzed by bismuth^{8b} or scandium triflate.^{8c}



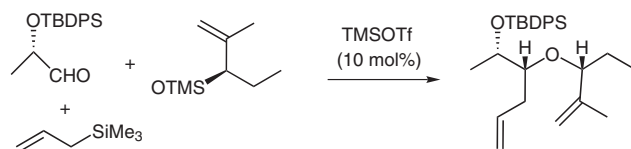
(F) Kiegiel and Jurczak reported the diastereoselective addition of allylic reagents to chiral carbon ketoimides derived from Oppolzer's sultam leading to the formation of a tertiary stereogenic centre.⁹



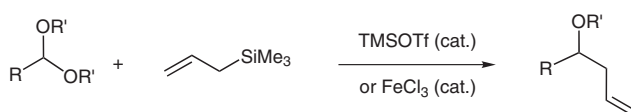
(G) Hwu and co-workers developed a sequential process involving allylation, free-radical cyclization and elimination reaction between carbonyl compounds and allyltrimethylsilane in acetic acid to give silicon-containing cyclopentanes with an *exo*-methylene unit in 52–71% yields.¹⁰



(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.¹¹



(I) A mild method for the chemoselective allylation of acetals has been developed using catalytic amounts of TMS triflate (5–20 mol%) in ionic liquids as solvents.¹² The same reaction can also be carried out by using FeCl₃ as catalyst.



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