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Trialkylsilyl Triflate Promoted Conjugate Addition of Allylstannes to α,β-Enones

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TRIALKYLSILYL TRIFLATE PROMOTED CONJUGATE ADDITION OF ALLYLSTANNES TO α,β-ENONES

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ABSTRACT: Trialkylsilyl triflates promote conjugate addition of allylstannes to α,β-enones to afford β-alkylated silyl enol ethers in high yields.

Because of the difficulty in conjugate addition of allyl cuprate reagents to α,β-enones,[1] Lewis acid promoted conjugate addition of allylsilanes to α,β-enones has become the method of choice.[2] Since allylstannes have similar or even enhanced chemical reactivities, as compared with allylsilanes,[3] allylation reactions of various electrophiles such as acetals[4] and carbonyl compounds[5] with allylstannes in the presence of Lewis acids have been reported.

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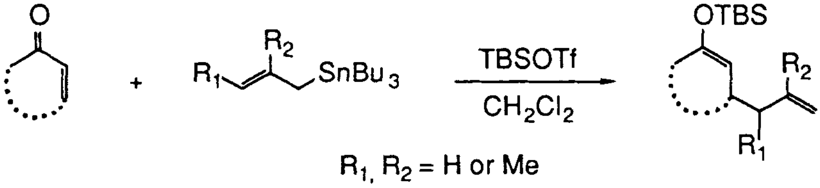
Lewis acids employed in the conjugate allylation of α,β-enones include bis(diethylaluminum)sulfate,[6] titanium tetrachloride,[7] and aluminum trichloride.[7] However, each method has several limitations. These methods provide δ,ε-enones and the low yields are realized with bis(diethylaluminum)sulfate.[6]

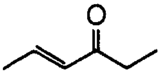
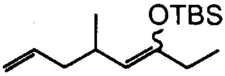
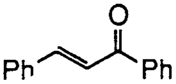
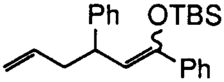
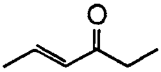
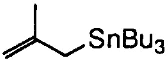
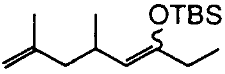
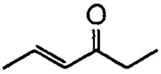
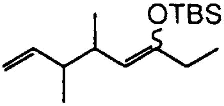
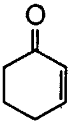
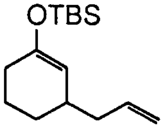
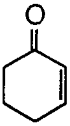
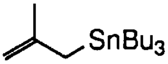
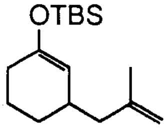
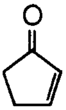
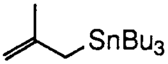
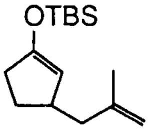
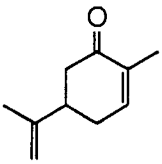
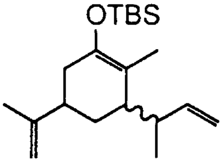
Recently, we have found that trialkylsilyl triflate is very effective in promoting conjugate addition of relatively unreactive alkynylzinc compounds to α,β-enones.[8] Based on the similar idea and previous reports,[6,7] we have investigated the possibility of allylation of α,β-enones with allylstannes in the presence of trialkylsilyl triflate, as shown in Scheme 1. Since the present method provides synthetically important β-allylated silyl enol ethers,[9] we believe that the method is much more advantageous than the previously reported methods in the regioselective α-functionalization of α,β-enones.



Scheme 1

Conjugate addition reaction of allylstannes to α,β-enones was initially attempted with other carbonyl activating agents such as trimethylsilyl chloride and tri-n-butyltin triflate and no successful results were obtained. Furthermore, it is noteworthy that conjugate addition of allylsilanes to α,β-enones in the presence of

Table 1. Conjugate Addition of Allylstannes to α,β–Enones

Enone	Allylstanne	Product	Yield (%)[a]
			82
			95
			94
			80
			85
			88(82)^b
			82
			88^c

[a] The yields refer to isolated products. [b] TMSOTf was employed.
[c] The stereochemistry has not been determined.

trimethylsilyl triflate (TMSOTf) in dichloromethane did not take place. However, reaction of allylstannes with α,β-enones proceeded cleanly in the presence of TMSOTf and the reaction occurred almost instantly at -78 °C in dichloromethane. For instance, reaction of 2-cyclohexen-1-one with equimolar amounts of methallylstannes and TMSOTf in dichloromethane at -78 °C for 10 min gave the desired product in 82% yield after silica gel column chromatographic separation. As shown in the table 1, the remaining reactions were carried out with t-butyldimethylsilyl triflate (TBSOTf) due to the better stability of the products. The present method works well with both cyclic and acyclic α,β-enones without yielding 1,2-addition products. However, the method failed with β-disubstituted α,β-enones like isophorone and no reaction occurred. The result obtained here is in sharp contrast with the previously reported method, in which conjugate addition of allylsilane to isophorone in the presence of titanium tetrachloride occurred smoothly.[2]

A typical procedure is as follows. To a solution of α,β-enone (1.0 mmol) and allylstanne (1.2 mmol) in dichloromethane (5 ml) at -78 °C was added TBSOTf (1.2 mmol). After being stirred at -78 °C for 10 min, the reaction was quenched with saturated sodium bicarbonate solution. Extraction with dichloromethane, solvent removal and silica gel column chromatographic purification afforded the product.

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