Sulfoniosilylation of α,β-Unsaturated Carbonyl Compounds. Facile Nucleophilic Substitution of 3-Trialkylsilyloxyalk-2-enylenesulfonium Salts

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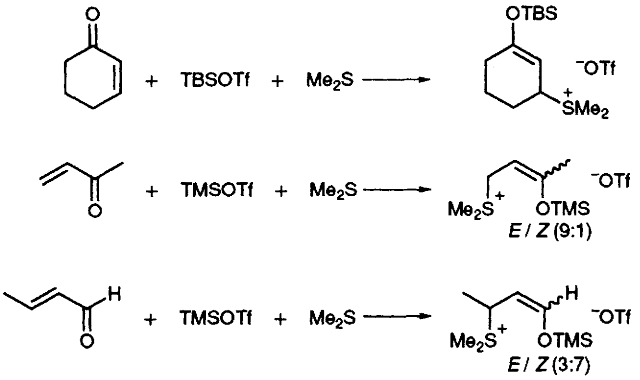
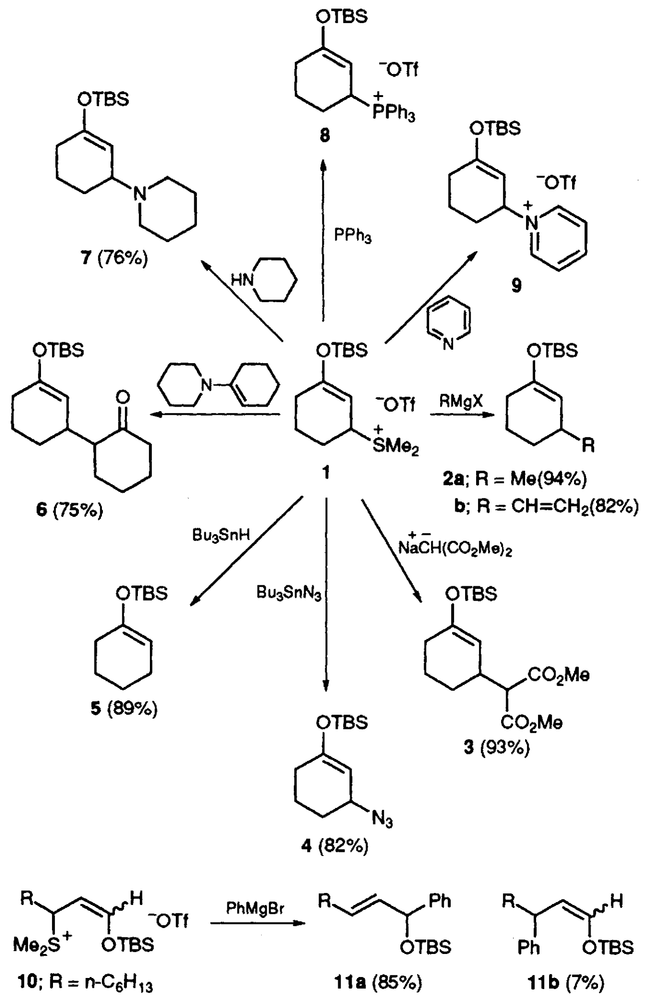
Sulfoniosilylation of α,β-enones and α,β-enals with trialkylsilyl triflate and dimethyl sulfide at −78 °C affords 3-trialkylsilyloxyalk-2-enylenesulfonium salts, which undergo facile nucleophilic substitution with various nucleophiles.

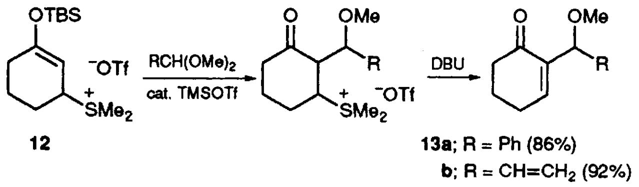
Sulfonium salts have been utilized mainly in the generation of sulfur ylides[1] and have limited use as leaving groups,[2] although nucleophilic addition of dialkyl sulfide to acrylic acid in the presence of HCl has been reported.[3] However, this reaction was unsuccessful with α,β-enones under similar conditions. We have investigated the possibility of sulfoniosilylation of carbonyl compounds to generate highly reactive 3-trialkylsilyloxyalk-2-enylenesulfonium salts and permit the introduction of a wide variety of nucleophiles at the β-position as well as α-functionalization.



Scheme 1 (TBS = *tert*-butyl dimethylsilyl; TMS = trimethylsilyl)



Scheme 2



Scheme 3

The sulfoniosilylation of α,β-enones was carried out with trialkylsilyl triflate (1.2 equiv.) and an excess of dimethyl sulfide (2–3 equiv.) in dichloromethane, tetrahydrofuran (THF), or diethyl ether at −78 °C, see Scheme 1. The formation of the sulfonium salts was determined by low-temperature ^{1}H NMR spectroscopy in $CDCl_3$ (−40 °C) or in [$^2H_8$]THF (−50 °C). The reaction proceeded cleanly *via* the 1,4-addition mode and when the reaction was conducted with methyl vinyl ketone, a 9 : 1 ratio of (*E*)- and (*Z*)-isomer was obtained in $CDCl_3$ at −40 °C. Also, simple dialkyl sulfides and tetrahydrothiophene could be successfully employed but diphenyl sulfide failed to undergo sulfoniosilylation owing to its low nucleophilicity. The sulfonium salts were thermally unstable and decomposed above −20 °C. Finally, similar results were obtained with α,β-enals and no 1,2-addition products were observed at −70 °C unlike pyridiniosilylation[4] and phosphoniosilylation reactions of α,β-enals.[5]

Nucleophilic substitution of 3-trialkylsilyloxyalk-2-enylene-sulfonium salts with various nucleophiles was studied using **1** as shown in Scheme 2. Typically, the reaction was carried out with 1.2 equiv. of nucleophile in THF at −70 °C and was almost instantaneous, yielding conjugate addition products of cyclohex-2-en-1-one in high yields.[6,7] Reaction of **1** with Grignard reagents in THF at −70 °C for 10 min afforded **2a** and **2b** in 94 and 82% yield, respectively. This two-step conversion corresponds to the 1,4-addition of Grignard reagents to α,β-enones. Treatment of **1** with the sodium salt of dimethyl malonate under similar conditions gave **3** in 93% yield. Similarly, **1** was easily displaced by tributyltin azide, tributyltin hydride, enamine and piperidine to afford **4**, **5**, **6** and **7** in high yields. Furthermore, **1** readily reacted with triphenylphosphine and pyridine to yield **8** and **9**, which were confirmed by ^{1}H NMR analysis. In the case of **10**, S_N2' reaction was predominant. Thus, treatment of **10** with phenyl magnesium bromide gave 85% of **11a** along with 7% of **11b**.

α-Alkoxyalkylation of α,β-enone was examined briefly with **12** as shown in Scheme 3.[4,8] Treatment of **12** with 1.1 equiv. of an acetal in the presence of 0.2 equiv. of TMSOTf in THF at −50 °C for 1 h, followed by the addition of 1,8-diazabicyclo[5.4.0]undec-7-ene gave **13** in high yield.

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