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Dehydration of α-Silylalcohols in the Reductive Conversion of Esters and Ketones into Alkenes

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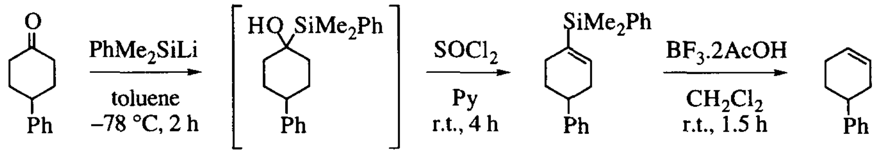
Abstract The conversion of esters and ketones into easily dehydrated α-silylated alcohols, and protodesilylation of the resultant vinylsilanes, gives alkenes under relatively mild acidic conditions.

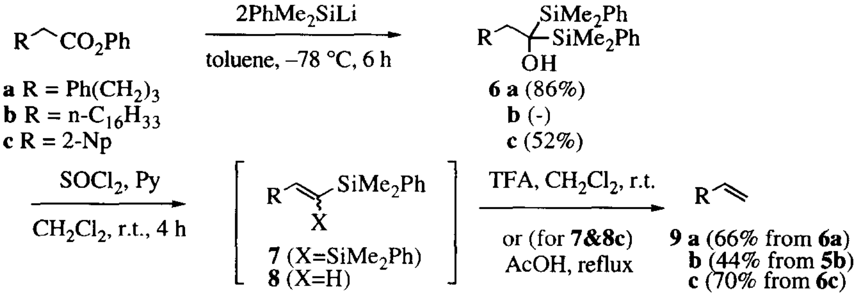
The acid-catalysed dehydration of a primary or even a secondary alcohol to give an alkene is a method for making alkenes, but it is not often used, because direct dehydration requires relatively forcing acidic conditions, towards which the alkene products are often not stable. The problem is usually avoided by sulfonylating the alcohol, or converting it into the corresponding halide, and inducing elimination with base.

We considered the possibility that alcohols having one or two α silyl groups might undergo dehydration to give vinylsilanes more easily than the dehydration of the corresponding alcohols having hydrogen atoms in place of the silyl groups. This was suggested by the observation that an α silyl group is intermediate between a hydrogen atom and an alkyl group in its capacity to stabilise a neighbouring carbocation.[1] α-Silyl alcohols can be made easily by treating a ketone with the phenyldimethylsilyllithium reagent.[2] If dehydration is easy, they will give vinylsilanes, which can readily undergo protodesilylation. The overall result will be the synthesis of an alkene under significantly milder conditions than would be needed in the absence of the silyl group. We illustrate the sequence using 4-phenylcyclohexanone **1**, which gave the mixture of alcohols **2** when treated with the silyllithium reagent in toluene. The selectivity for attack on the carbonyl group, as distinct from attack on the α-proton leading to an enolate, is high, and in our experience usually a little higher in toluene than in THF. The alcohols **2** can be isolated in 85% yield, but the dehydration could be carried out directly on the mixture by adding thionyl chloride and pyridine,[3] which gave the vinylsilane **3** in 90% yield in one pot. Protodesilylation of the vinylsilane gave the alkene **4** under relatively mild acidic conditions in 95% yield. Although we did not carry out the trivial hydrogenation of the double bond, it would have given overall the same result as a Wolff-Kishner or Clemmensen reaction, but under significantly different conditions.

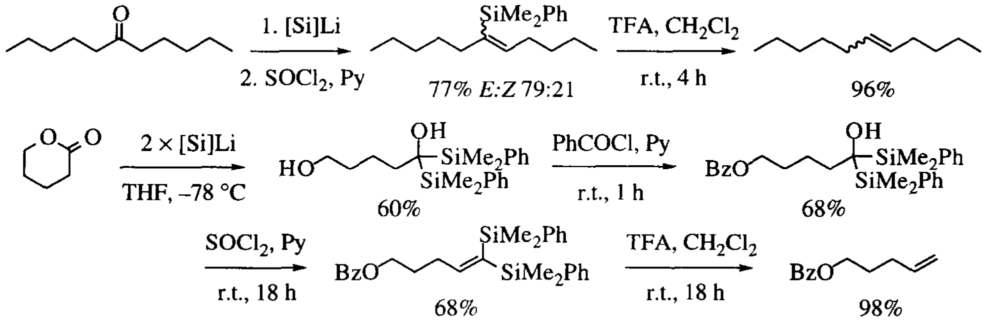


1 **2** **3** (90%) **4** (95%)

The problem dehydrating a primary alcohol is even worse, and Grieco's sequence using the thermal elimination of a selenoxide is often used to overcome the difficulty.[4] Again we considered that having two silyl groups α to the hydroxyl group ought to make the dehydration easier. Indeed, we had already discovered that thionyl chloride induced elimination in this situation,[5] and we now show that the whole sequence, attack by silyllithium reagent, dehydration and protodesilylation, can be used to convert an ester group into a terminal vinyl group. Following our earlier work, the esters **5** gave the disilyl alcohols **6**, and dehydration gave the vinyldisilanes **7**, contaminated with small amounts of the corresponding vinylsilanes **8**. The formation of a mixture was of no consequence in the present context, and isolation of the intermediates was unnecessary, since protodesilylation removed the silyl groups from both compounds to give the alkenes **9** with overall yields based on the esters **5** of 36-57%.



Here are two other examples of these sequences, starting with a ketone and a lactone:



but we were not successful in converting either acetophenone into styrene or *N*-methoxycarbonylethylpiperidine into *N*-allylpiperidine, because the protodesilylations did not work, the former giving mixtures, and the latter no reaction at all.

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