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A Simple One Pot Procedure For The Generation of Homoallylic Alcohols From Acetals And Amino Acetals

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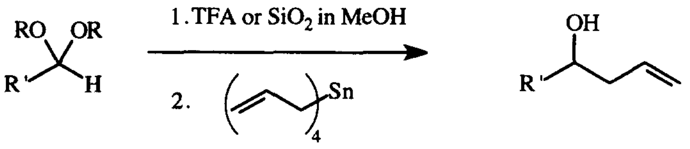
Abstract: Treatment of acetals (**1** and **2**) and amino acetals (**3-5**) with either trifluoroacetic acid (TFA) or silica gel followed by tetraallyltin gave excellent yields of the corresponding homoallylic alcohols (68 - 100%). © 1997 Elsevier Science Ltd.

The allylation of carbonyl compounds, especially aldehydes is an extremely useful transformation in synthetic organic chemistry.[1] A variety of allylic metals have been used, with allyltin, allylsilane and more recently allylgermane being investigated. [2] We recently reported the solvent promoted addition of tetraallyltin to aldehydes.[3]

A significant drawback in this type of reaction, is that the aldehydes must be readily available and more importantly stable. This is especially the case in the use of amino acids as sources of chiral aldehydes.[4] As such we have investigated the possibility of a "one-pot" conversion of amino acetals and acetals to the corresponding homoallylic alcohols (Scheme 1).



R = Ph, $PhCH_2$, $H_2NCH_2CH_2$, $H_2N(CH_2)_4$, Boc-D-$NHCHCH_3$

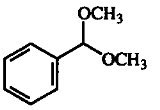
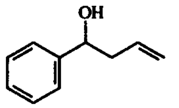
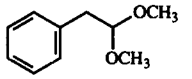
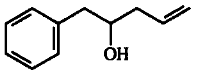
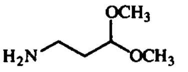
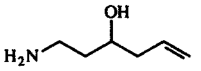
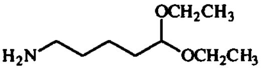
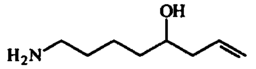
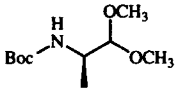
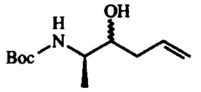
Scheme 1

Thus, in a typical reaction, the acetal (10 mmol) in methanol (10 mL) containing 0.25 equivalents of tetraallyltin was stirred at 30°C overnight (typically 12-20 hrs). The reaction mixture subjected to an extractive work up to yield essentially pure homoallylic alcohols, as shown in table 1.

As can be seen from entries 1, 3, 5, 7, and 9 excellent yields are obtained by the use of TFA as the acetal cleaving reagent. With SiO_2 the reaction required the addition of ca 0.5 mL of H_2O to ensure that an acceptable rate of reaction was obtained. Generally the SiO_2 reaction gave marginally lower product yields. Akiyama and Iwai have also commented on the addition of H_2O to the solvent in the tetraallylgermane scandium (III) mediated allylation reaction, although in that instance a reduction of reaction rate was observed.[5] Entries 7 and 8 indicate that the procedure works equally well for methyl and ethyl acetals.

To verify the validity of this method for the allylation of amino aldehydes, the amino acetal generated from Boc-D-Ala was subjected to these reaction conditions. It was found necessary in this instance to add a second equivalent of TFA (the first being consumed in the removal of the Boc protecting group), this was not observed in the SiO_2 reaction.

Table 1. Yields Of Homoallylic Alcohols Upon Treatment With Either SiO_2 Or TFA And Tetraallyltin. Yields quoted are those of isolated products.

Entry	Compound	Product	TFA (%)	SiO_2 (%)
1, 2			100	74
3, 4			72	68
5, 6			99	68
7, 8			97	79
9, 10			84[a]	78

[a]With TFA only the free amino alcohol is recovered. *syn* : *anti* 68 :32

Thus, the one pot synthetic procedure presented herein represents an elegant route to homoallylic alcohols from readily available, stable precursors.[6] We believe that this also represents the first direct allylation of acetals by an allylic metal species.

Acknowledgments

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References and Notes

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6. All new compounds returned satisfactory analysis.

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