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TRIMETHYLSILYL-HALIDE-MEDIATED CONJUGATED ADDITION
TO ALLYLIC ACETALS

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ABSTRACT: Trimethylsilyl chloride can effect the conjugated addition of NaX (X = Br, I, SCN) to α,β -unsaturated acetals and ketals without deprotection of the carbonyl group.

The conversion of acetals and ketals into the carbonyl compounds with trimethylsilyl iodide (TMSI) is a facile procedure giving high yields under mild and neutral conditions¹. Experimental procedures using in-situ generated TMSI from trimethylsilyl chloride and sodium iodide have been successfully applied for this conversion². However, α -iodo ethers were obtained from the reaction of 1,3-dioxolanes with TMSI² and ethylene ketals only gave mixtures of products. Recently, ring-opening reactions were observed in the cleavage of dimethoxytetrahydrofurans and dimethoxydihydrofurans³.

We have found that the reaction of 3,3-dimethoxy-1-propene (1) with in-situ generated TMSI (from TMSCl and KI) in dry acetonitrile unexpectedly yields 1-iodo-3,3-dimethoxypropane (2).

Similarly, using NaBr or KSCN instead of KI, a formal anti-Markovnikov addition of HBr or HSCN was achieved. Further examples (see Table, entries 5 and 6) show that addition to the olefinic bond is faster than dioxolane cleavage to α -iodo ethers and that the conversion also proceeds well in the case of an allylic ketal (entry 7).

Table: β -Functionalized acetals from allyl acetals using TMSCl

	Allyl acetal	Salt	Temp., °C	Time, min	Product ^a	Yield ^b , %
1		KI	22	90		60 (70) ^c
2		NaBr	22	90		63
3		KSCN	-20	90		40
4		NaBr	22	60		51
5		KI	22	90		65
6		NaBr	22	90		55
7		NaBr	0	45		52
8		NaBr	0	60		35 (60) ^c
9		NaI	-30	30		90

a. All products gave correct NMR data and elemental analyses and/or mass spectral data, or were identical with samples prepared independently.

b. Isolated yield.

c. Yield by NMR.

The use of the more reactive, salt-free TMSI leads to low yields. The use of larger quantities of TMSCl , higher reaction temperatures or longer reaction times results in deketalisation (e.g. entry 7: 60 % yield of 4-bromo-2-butanone after 75 min at 22 °C) and the formation of product mixtures.

2-Haloethyl acetals and dioxolanes have found widespread application as 3-carbon synthons and some of them are prepared by multistep procedures⁴. The method presented here offers the possibility of β -functionalization of protected carbonyl compounds and provides a mild alternative to existing procedures for the preparation of acrolein derivatives⁵.

Procedure

A mixture of 2.57 g (25 mmol) of NaBr , 1.7 ml (125 mmol) of TMSCl and 0.5 g of 4Å sieves in 20 ml of dry CH_3CN was stirred under nitrogen for 15 minutes. Subsequently, 1.28 g (12.5 mmol) of 3,3-dimethoxy-1-propene dissolved in 5 ml of CH_3CN was added and the mixture was stirred at 22 °C for 90 minutes. After an aqueous work-up and distillation (bulb-to-bulb) of the crude product, 1.45 g (63 %) of pure 1-bromo-3,3-dimethoxypropane (b.p. 125 °C; 1 mm) was obtained.

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