Pergamon

Tetrahedron Letters, Vol. 35, No. 13, pp. 2027-2030, 1994
Elsevier Science Ltd
Printed in Great Britain
0040-4039/94 $6.00+0.00

0040-4039(94)E0211-F

A One-step and Chemoselective Conversion of Silyl-protected Alcohols into the Corresponding Acetates

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Abstract: A reagent system of acetyl bromide combined with a catalytic amount of tin(II) bromide cleaves readily trialkylsilyl ethers to give the corresponding acetates in high yields under very mild conditions.

Silyl ethers have become one of the most popular protective groups for a hydroxylic function and a great variety of silyl protective groups of every situational choice has now been devised and utilized in synthetic sequences of complex organic compounds.[1] In these synthetic sequences, it is frequently needed to transform an existing protective group to another one pertinent to the following steps, and this usually calls for two separate steps, i.e. a deprotection and a protection-anew.[2] It will therefore be of great benefit in view of time and material savings to have means of one-step transformations between protective groups.

From this viewpoint, we have already demonstrated a direct conversion of benzyl- and *p*-methoxybenzyl-protected alcohols to the corresponding acetates[3] and methoxymethyl ethers,[4] respectively, without any manipulation to detach the former protective groups. Now we wish to report an expedient procedure for a direct conversion of silyl-protected alcohols into the corresponding acetates under very mild conditions.[5]

In the first place, we examined the reaction of 1-trimethylsiloxy-2-phenylethane with acetyl bromide in the presence of catalytic amount of tin(II) bromide according to the procedure reported in the previous paper.[3] After a screening of various reagent systems, we found that the employment of 1.5 equivalents of acetyl bromide in the presence of 0.05 equivalent of tin(II) bromide gave the best result as shown in Table 1.

Table 1. The Effect of Various Reagent Systems on the One-step Conversion of TMS Ether into Acetate.

$$\mathrm{Ph(CH_2)_2OTMS} \xrightarrow[\mathrm{CH_2Cl_2\ /\ r\ t}]{\mathrm{AcX\ (150\ mol\%)\ -\ SnX_2\ (5\ mol\%)}} \mathrm{Ph(CH_2)_2OAc}$$

Run	AcX - SnX$_2$	Time / min	Yield[a] / %
1	AcBr - SnBr$_2$	5	93
2	AcBr - SnBr$_2$	20	94
3	AcBr	20	87
4	AcCl - SnCl$_2$	20	90
5	AcCl	20	38
6	AcBr - Sn(OTf)$_2$	20	83

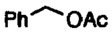
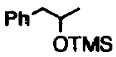
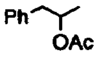
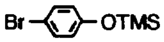
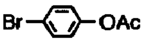
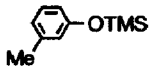
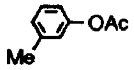
a) Isolated yield from TMS ether.

The reaction was conducted with various trimethylsilyl (TMS) ethers of primary, secondary, and phenolic alcohols and the results are summarized in Table 2. Although the reaction without tin(II) bromide (method B) showed considerable success, the reaction in the presence of a catalytic amount of tin(II) bromide (method A) gave better results: corresponding acetates were obtained in higher yields and in shorter reaction time.[6] Using this method, all the TMS ethers tried were transformed into the corresponding acetates in good to excellent yields under very mild reaction conditions.[7]

Table 2. Synthesis of Various Acetates from TMS Ethers[a)]

$$\mathrm{ROTMS} \xrightarrow[\mathrm{CH_2Cl_2\,/\,r\,t\,/\,20\ min}]{\text{Method A or B}} \mathrm{ROAc}$$

Method A : AcBr (150 mol%) - $SnBr_2$ (5 mol%)
Method B : AcBr (150 mol%)

Run	ROTMS	ROAc	Yield[b)] / % Method A	Yield[b)] / % Method B
1			77	84
2			94	87
3			95 (5 min)	93
4			94	92
5			97	88
6			95	87
7			95	84 (60 min)

a) Each product gave satisfactory ^1H NMR and IR spectra. b) Isolated yield.

We have also found that alkyl triethylsilyl (TES) ethers, alkyl *tert*-butyldimethylsilyl (TBDMS) ethers, and alkyl *tert*-butyldiphenylsilyl (TBDPS) ethers also undergo this direct conversion to the corresponding acetates in high yields as shown in Table 3.

The reaction was similarly effective to polysilyl ethers. As shown in Table 4, all the trimethylsiloxy, triethylsiloxy, and *tert*-butyldimethylsiloxy functions in the polyethers were readily converted into acetoxyl groups in good to excellent yields. Furthermore, reaction of sugar derivatives with this reagent system was tried and gave very good results as well. The corresponding tetra-acetate was obtained efficiently without concomitant substitution of alkoxyl by bromide at the anomeric position as described in the previous paper[3] (Runs 3 and 4). In the case of Run 5, transformation of silyl ethers with concomitant acetylation of free hydroxyl groups in the same molecule has occurred.

Table 3. One-step Conversion of TES, TBDMS, and TBDPS Ethers into Acetates [a]

$$ROSiR_3 \xrightarrow[CH_2Cl_2\ /\ r\ t]{AcBr\ (150\ mol\%)\ -\ SnBr_2} ROAc$$

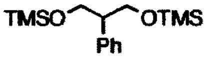
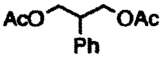
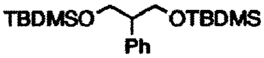
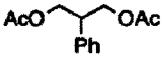
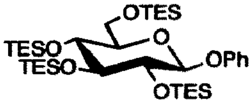
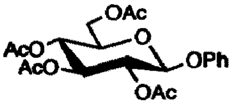
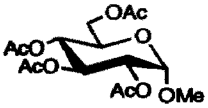
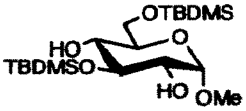
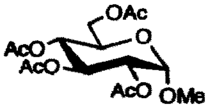
(TES = $SiEt_3$, TBDMS = Si^tBuMe_2, TBDPS = Si^tBuPh_2)

Run	$ROSiR_3$	$SnBr_2$ / mol%	Time / h	Yield[b] / %
1		5	0.3	87
2		5	0.3	82
3		0	2	95
4		5	0.3	100
5		0	1	77
6		5	0.3	84
7		5	24	82
8		5	3[c]	89
9		5	24	67
10		5	3[c]	78

a) Each product gave satisfactory ^1H NMR and IR spectra. b) Isolated yield.
c) 1,2-Dichloroethane was used in place of dichloromethane as a solvent.

Table 4. Synthesis of Various Polyacetates from Polysilyl Ethers [a]

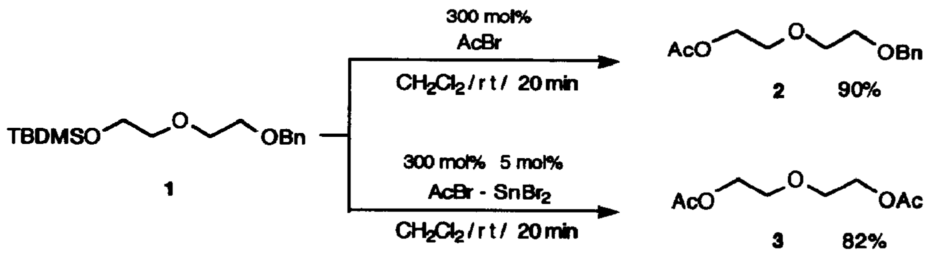
$$\text{Polysilyl Ether} \xrightarrow[CH_2Cl_2\ /\ r\ t]{AcBr\ -\ SnBr_2} \text{Polyacetate}$$

Run	Polysilyl Ether	Polyacetate	AcBr / mol%	$SnBr_2$ / mol%	Time / min	Yield[b] / %
1			400	5	20	83
2			400	5	20	76
3			600	10	20	92
4			600	10	20	96
5			600	10	60	86

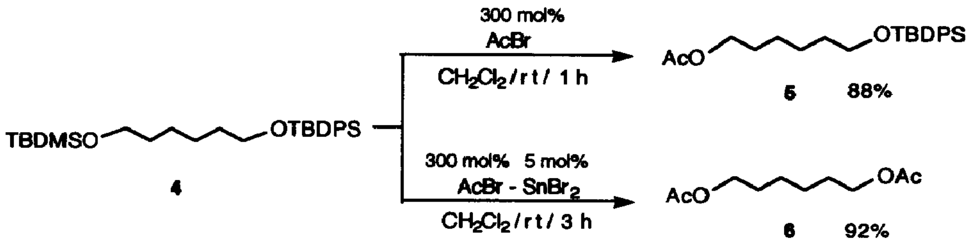
a) Each product gave satisfactory ^1H NMR and IR spectra. b) Isolated yield.

Chemoselective conversion of TBDMS ether into acetate in the presence of less reactive benzyl ether was demonstrated when the reaction was carried out without tin(II) bromide (Eq. 1). A similar but more subtle chemoselectivity between TBDMS ether and TBDPS ether was seen in Eq. 2. Reaction of **4** having both

TBDMS and TBDPS ethers with acetyl bromide in the absence of tin(II) bromide afforded the monoacetate **5** with TBDPS ether function unchanged chemoselectively. In both cases, the same reaction in the presence of tin(II) bromide afforded the corresponding diacetates in high yields.



(1)



(2)

The direct conversion of silyl ethers into acetates described here provides a new and convenient method for the synthesis of acetates from silyl ethers. Further investigations on the direct conversions of other protective groups are now in progress.

References and Notes

1. Greene, T. W.; Wuts, P. G. M. in *Protective Groups in Organic Synthesis*, 2nd Ed., John Wiley & Sons : New York, **1991** ; p 68 and p160.
2. For example, see: Danishefsky, S. J.; Liu, K. K.-C. *J. Am. Chem. Soc.*, **1993**, 115, 4933.
3. Oriyama, T.; Kimura, M.; Oda, M.; Koga, G. *Synlett*, **1993**, 437.
4. Oriyama, T.; Kimura, M.; Koga, G. *Bull. Chem. Soc. Jpn.*, in press.
5. A couple of procedures for a one-step conversion of silyl-protected alcohols into acetates are reported. (a) $FeCl_3$-Ac_2O, see: Ganem, B.; Small, Jr., V. R. *J. Org. Chem.*, **1974**, 39, 3728. Danishefsky, S. J.; Mantlo, N. *J. Am. Chem. Soc.*, **1988**, 110, 8129. (b) Pyridine-Ac_2O-AcOH or MeOH-AcOH, see: Fuchs, E.-F.; Lehmann, J. *Chem. Ber.*, **1974**, 107, 721. (c) $ZnCl_2$-AcCl, see: Kim, S.; Lee, W. J. *Synth. Commun.*, **1986**, 16, 659.
6. The following experimental procedure is typical: a dichloromethane (1.0 ml) solution of acetyl bromide (94 mg, 0.76 mmol) was added dropwise to a suspension of anhydrous tin(II) bromide (7.3 mg, 0.026 mmol) and 2-phenyl-1-trimethylsiloxyethane (96 mg, 0.49 mmol) in dichloromethane (1.5 ml) at room temperature under argon atmosphere. The resultant solution was stirred for 20 min at room temperature. The reaction mixture was quenched with a phosphate buffer (pH 7). The organic materials were extracted with dichloromethane (3 x 15 ml) and combined extracts were washed with brine and dried over anhydrous sodium sulfate. The solvent was evaporated and 2-phenylethyl acetate (76 mg, 94%) was isolated by thin layer chromatography on silica gel.
7. The complete retention of configuration was observed when the reaction was conducted with trimethylsilyl ether of an optically active secondary alcohol: (*S*)-2-trimethylsiloxyoctane (96%ee) obtained by silylation of (*S*)-2-octanol gave (*S*)-2-acetoxyoctane (96%ee) in 80% yield.

(*Received in Japan* 24 *November* 1993; *accepted* 13 *January* 1994)