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A NOVEL METHOD FOR DIRECT CONVERSION OF TETRAHYDROPYRANYL ETHERS INTO t-BUTYLDIMETHYLSILYL ETHERS WITH t-BUTYLDIMETHYLSILYL TRIFLATE AND DIMETHYL SULFIDE

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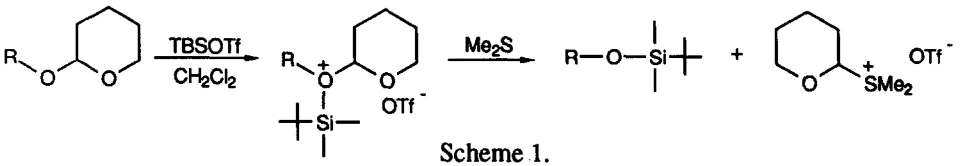
Summary: Direct conversion of THP ethers into TBS ethers has been achieved with TBSOTf and dimethyl sulfide in dichloromethane.

While examining methods for β-functionalization of α,β-unsaturated acetals,[1] we were originally interested in the mechanistic aspects of the acetal cleavage reaction[2] with trialkylsilyl triflate. Furthermore, in connection with our previous result on selective removal of tetrahydropyranyl (THP) ethers in the presence of t-butyldimethylsilyl (TBS) ethers,[3] we have studied the possibility of converting THP ethers into TBS ethers to achieve synthetically important direct conversion as well as to clarify the mechanistic aspects of the acetal cleavage reaction. Reaction of the phenethyl THP ether with an equimolar amount of t-butyldimethylsilyl triflate (TBSOTf) in dichloromethane at -78 °C for 30 min did not afford the phenethyl TBS ether, indicating against a common oxocarbenium ion intermediate. The involvement of the oxonium intermediate has been suggested by recovering the starting material in 80% yield when the reaction mixture was treated with aqueous potassium carbonate and further strengthened by treating the reaction mixture with dimethyl sulfide to give the phenethyl TBS ether.[4] This finding seems to be very important in understanding mechanistic and stereochemical aspects in the chiral acetal cleavage reaction.[5,6]

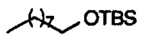
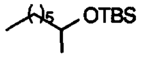
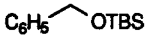
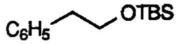
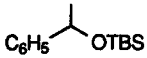
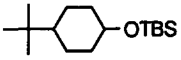
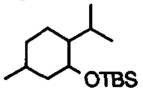
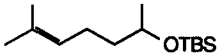
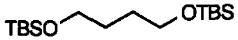
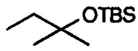
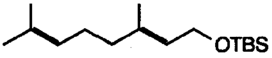


Scheme 1.

The present method is based on (i) exclusive exocyclic oxygen attack of THP ethers by TBSOTf,[7] (ii) the formation of an oxonium intermediate and (iii) its displacement with dimethyl sulfide to generate TBS ether,[8] as shown in Scheme 1.

Table 1 shows some experimental results and illustrates the efficiency and the scope of the present method. Primary and secondary alkyl or benzylic THP ethers worked well, yielding the corresponding TBS ethers in high yields. However, the present method reaches limits with allylic and tertiary alkyl THP ethers.

Table 1. Conversion of ROTHP into ROTBS with TBSOTf and Me_2S.

Product	Yield, %	Product	Yield, %
	95		91
	94		91
	93		90
	97		92
	94		96
	23		24

The typical procedure is illustrated as follows. To a solution of the THP ether (1.0 mmol) in CH_2Cl_2 (5 ml) at -50 °C was added TBSOTf (1.3 mmol). Stirring for 30 min was followed by the addition of Me_2S (3.0 mmol) at -50 °C.[9] After being stirred for 1 h at -50 °C, the reaction mixture was treated with an excess amount of Et_3N[10] and the following usual workup gave the TBS ether.[11]

References and Notes

1. S. Kim and Y. C. Kim, *Synlett*, 115 (1990) and *Tetrahedron Lett.*, in press.
2. T. Tsunoda, M. Suzuki and R. Noyori, *Tetrahedron Lett.*, **21**, 71 (1980); S. Murata, M. Suzuki and R. Noyori, *Tetrahedron*, **44**, 4259 (1988).
3. S. Kim and J. H. Park, *Tetrahedron Lett.*, **28**, 439 (1987).
4. During our studies, the similar result was reported. S. E. Denmark and T. M. Willson, *J. Am. Chem. Soc.*, **111**, 3475 (1989).
5. Y. Yamamoto, S. Nishii and J-I, Yamada, *J. Am. Chem. Soc.*, **108**, 7116 (1986) and references cited therein.
6. Chiral cyclic acetal cleavage reactions with TMSOTf did not occur due to the steric bulkiness of TMSOTf.
7. R. B. Gupta and R. W. Franck, *J. Am. Chem. Soc.*, **109**, 6554 (1987).
8. A. C. West and C. Schuerch, *J. Am. Chem. Soc.*, **95**, 1333 (1973). Ph_3P could be used instead of Me_2S but the yields were slightly decreased. However, pyridine and Et_3N were ineffective.
9. Since Me_2S does not react with TBSOTf, the order of mixing the reagents is not important.
10. The addition of Et_3N is beneficial to obtain optimal yields of TBS ethers.
11. This work was financially supported by KOSEF and experimenal assistance by Dr. J.H. Park is acknowledged.

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