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METALLOID DERIVATIVES FOR SYNTHESIS: MONODERIVATIZATION OF SYMMETRIC DIOLS

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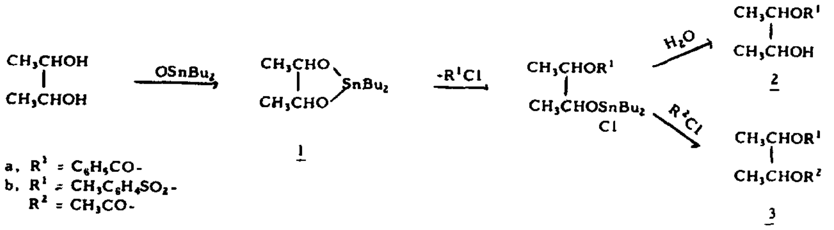
Summary: The monoderivatization of symmetric diols by condensation of their stannoxanes with activated halides is described.

The monoderivatization of symmetric, difunctional substrates is quite a common synthetic problem. A solution to this problem has recently been introduced by Leznoff et al.[1], who applied insoluble polymer supports as monoblocking agents. We wish to describe a different approach which is based on the use of tin as activating agent and template. The latter combines the two functional groups of the substrates, e.g. diols, into cyclic intermediates, e.g. stannoxanes[2], which are well defined and readily available compounds. The cyclic arrangement of the latter renders the two functional groups interdependant allowing their non-symmetric derivatization.

Specifically, 2,3-butanediol has been reacted with dibutyl tin oxide to provide the known stannoxane 1[2]. Condensation of the latter with one equivalent benzoylchloride or tosyl chloride and subsequent hydrolysis gave the corresponding hydroxy benzoate 2a[3] or hydroxy tosylate 2b in quantitative yields.



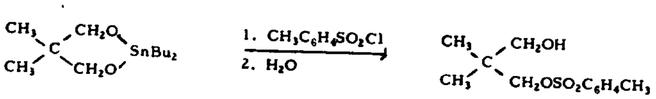
The prefered procedure involves treatment of 1.0 g($3.13.10^{-3}$mol) stannoxane 1 in 20 ml chloroform with 0.36 ml ($3.13.10^{-3}$mol) benzoyl chloride or 596 mg ($3.13.10^{-3}$mol) tosyl chloride under reflux for 1 hr. Then 5 ml 4 % aqueous dioxane is added and reflux continued for 1 hr. Dilution of the organic phase with chloroform and washing with aqueous bicarbonate and water provides the hydroxy benzoate 2a or hydroxy tosylate 2b respectively.

The same approach could also be applied for the preparation of non-symmetric diesters by consecutive reaction with two different halides. Treatment of the stannoxane 1 with one equivalent benzoyl chloride followed by one equivalent acetyl chloride afforded the non-symmetric diester 3a without contamination of the symmetric derivatives. All products were identified by their spectroscopic properties, the nmr data being summarized in the table below.

Table: Chemical Shifts of Non-Symmetric Butanediol Derivatives[4]

Compound	$C\underline{H}_3$-	$C\underline{H}OR^2$	$C\underline{H}OR^1$	$C\underline{H}_3$-	$CHO\underline{R}^2$	$CHO\underline{R}^1$
<u>2a</u> (R^2 = H)	1.18 (d)	3.95(m)	5.05(m)	1.42(d)	3.2(s)	7.3(m) 7.85(m)
<u>2b</u> (R^2 = H)	1.02 (d)	3.90(m)	4.5(m)	1.10(d)	3.5(s)	2.21(s) 7.4 (AB q.)
<u>3a</u> (R^2 = CH_3CO)	1.3(d)	5.2(m)	5.2(m)	1.35(d)	2.0(s)	7.2(m) 7.8(m)

This reaction is not limited to vicinal diols. Monoderivatization of a 1,3-diol, 2,2-dimethyl-1,3-dihydroxy propane to the corresponding tosylate <u>5</u> [5] was realized by treatment of the cyclic stannoxane <u>4</u>[2] with tosyl chloride, as illustrated underneath.



<u>4</u> <u>5</u>

The derivatization of symmetric diols to hydroxy esters, hydroxy tosylates and non-symmetric diesters demonstrates the potential of the approach. The key of the method relies on the interdependance of the geminal tin-oxygen bonds in the cyclic stannoxanes. Attack on the first bond greatly deactivates the second one due to the presence of the electronegative chlorine substituent. The second bond remains thus intact towards the first equivalent of reagent and is only cleaved by the second one. This method is thereby based on a kinetic effect, while the polymer approach[1] makes use of the dilution principle. Experiments on the scope and limitations of the method are under current investigation as are studies on its potential applications to natural product chemistry.

References

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4. The spectra have been measured on a Varian A-60 instrument. The chemical shifts are relative to internal tetramethyl silane in $CDCl_3$ solution.
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