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ACTIVATION AND SYNTHETIC APPLICATIONS OF THIOSTANNANES. A NEW METHOD FOR SYNTHESIS OF THIO- AND SELENOGLYCOSIDES

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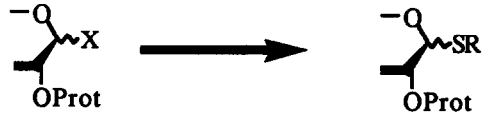
ABSTRACT. Exposure of thiostannane to acetyl or methyl glycosides in the presence of a catalytic amount of $Bu_2Sn(OTf)_2$ provides thioglycosides in good yields. Selenoglycosidation is achieved in a like manner by use of selenostannane.

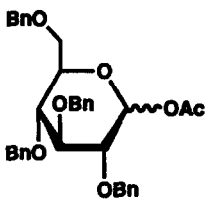
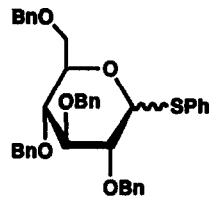
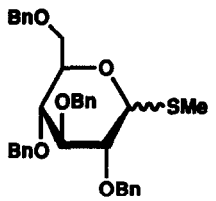
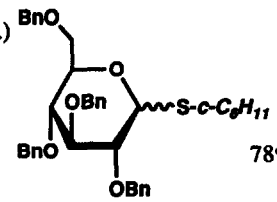
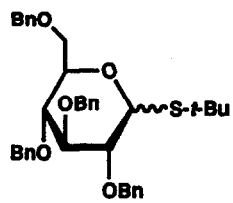
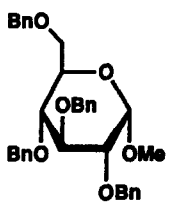
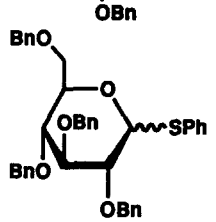
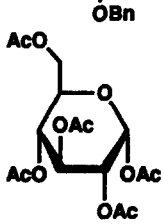
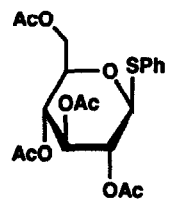
Thioglycosides have received extensive attention as versatile glycosyl donors which are subject to nucleophilic attack when converted into glycosyl halides[1] or exposed to thiophiles.[2] Even electrophilic[3] and radical[4] processes have also been disclosed. Various methods were reported to prepare these compounds.[5] These methods, though being considerably efficient, suffer from some limitations. In particular, excessive thioalkoxylation occasionally takes place to convert the resulting thioglycosides further to polysulfurized products. Ogawa et al. overcome this drawback by reducing the nucleophilicity of thioalkoxylating reagent: thiostannanes were employed in the presence of an equivalent amount of $SnCl_4$.[6]



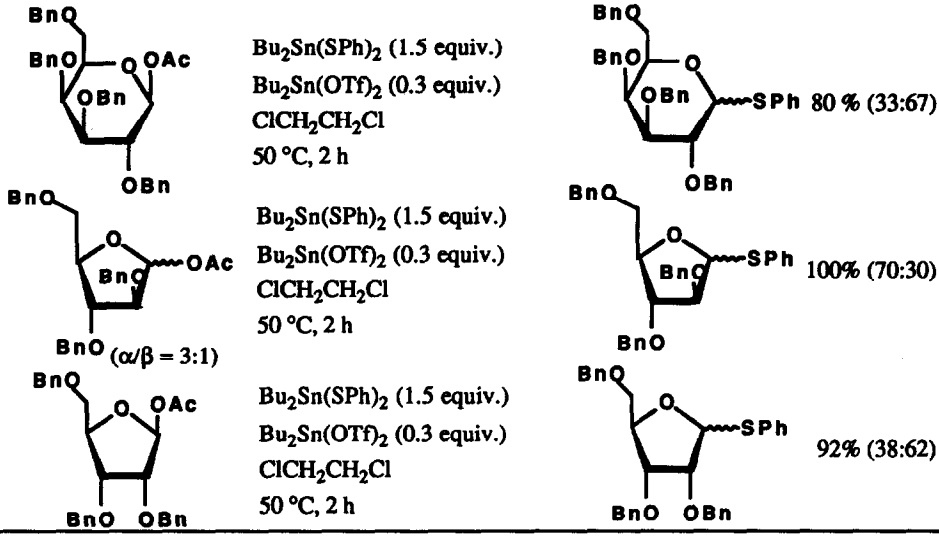
We have disclosed that thiostannanes effect thioalkoxylation of acetals in the presence of Lewis acid.[7] Moreover, organotin triflates have proved to be among others a mild Lewis acid to enable various selective reactions.[8] We report here that thiostannanes when coupled with *a catalytic amount of $Bu_2Sn(OTf)_2$* serve quite efficiently for thioglycosidation of acetyl and methyl glycosides. In addition, this method permits selenoglycosidation as well. Selenoglycosides are unique in that they are able to generate glycosyl radicals easily[9] and to work as versatile glycosyl donors[10] but rather difficult to prepare on account of their instability.

A 1,2-dichloroethane solution of acetyl glucoside ($\alpha:\beta$ = 67:33) (1 equiv.), $Bu_2Sn(SPh)_2$ (1.5 equiv.), and $Bu_2Sn(OTf)_2$ (0.3 equiv.) was heated at 50 °C for 30 min. Usual workup furnished phenylthio glucoside in 74% yield ($\alpha:\beta$ = 62:38). Note that Bu_3SnOTf is not enough acidic to give only 32% yield under analogous conditions. Table 1 shows whole results. Apparently, a wide variety of thiostannanes and glycosides are employable and reasonable yields are obtained in all cases.

Table 1. Thioglycosidation of acetyl and methyl glycosides by thiostannane-organotin triflate method

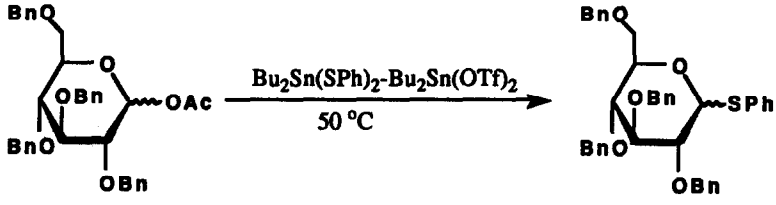
acetyl or methyl glycoside	conditions	thioglycoside	yield (α:β)
 α/β = 67:33	$Bu_2Sn(SPh)_2$ (1.5 equiv.) $Bu_2Sn(OTf)_2$ (0.3 equiv.) $ClCH_2CH_2Cl$ 50 °C, 0.5 h		74% (62:38)
	$Bu_2Sn(SMe)_2$ (1.5 equiv.) $Bu_2Sn(OTf)_2$ (0.3 equiv.) $ClCH_2CH_2Cl$ 50 °C, 4 h		65% (62:38)
	$Bu_2Sn(S\text{-}c\text{-}C_6H_{11})_2$ (1.5 equiv.) $Bu_2Sn(OTf)_2$ (0.3 equiv.) $ClCH_2CH_2Cl$ 50 °C, 4 h		78% (68:32)
	$Bu_2Sn(S\text{-}t\text{-}Bu)_2$ (1.5 equiv.) $Bu_2Sn(OTf)_2$ (0.3 equiv.) $ClCH_2CH_2Cl$ 50 °C, 4 h		75% (76:24)
	$Bu_2Sn(SPh)_2$ (1.5 equiv.) $Bu_2Sn(OTf)_2$ (0.3 equiv.) $ClCH_2CH_2Cl$ 90 °C, 4 h		63% (65:35)
	$Bu_2Sn(SPh)_2$ (1.5 equiv.) $Bu_2Sn(OTf)_2$ (0.3 equiv.) $ClCH_2CH_2Cl$ 90 °C, 4 h		77% (0:100)

(Table 1 continued)



Another notable feature of the thiostannane-organotin triflate method is illustrated in Scheme 1. Stereochemistry of glycosidation reaction is usually dependent on solvent.[11] The present method surprisingly provides nearly identical stereochemical outcome for the thioglycoside irrespective of the solvent polarity.[12]

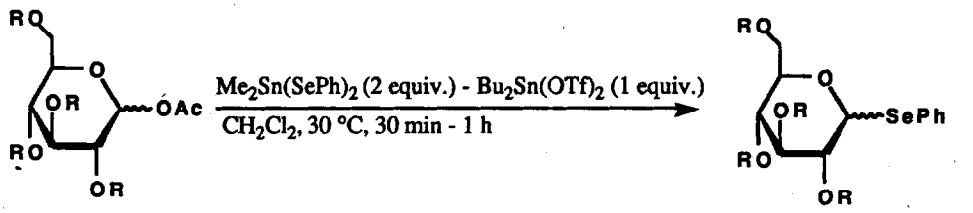
Scheme 1



$ClCH_2CH_2Cl$, 0.5h	74%, α/β = 62:38
toluene, 6h	63%, α/β = 71:29
THF, 3h	62%, α/β = 67:33
CH_3CN, 3h	14%, α/β = 62:38

Finally, selenoglycosidation was effected (Scheme 2). A dichloromethane solution of acetyl glucoside (1 equiv.), $Me_2Sn(SePh)_2$ (2 equiv.), and $Bu_2Sn(OTf)_2$ (1 equiv.) was stirred at 30 °C. After 1 h, 70% of the desired selenoglucoside was produced. The methyl derivative was obtained in 73% yield after 30 min. The simple operation obviously provides a new, practical route for selenoglycosides.

Scheme 2



R = CH_2Ph 70% (α:β = 89:11)

= Me 73% (α:β = 88:12)

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12. No isomerization of the product was observed under the reaction conditions.

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