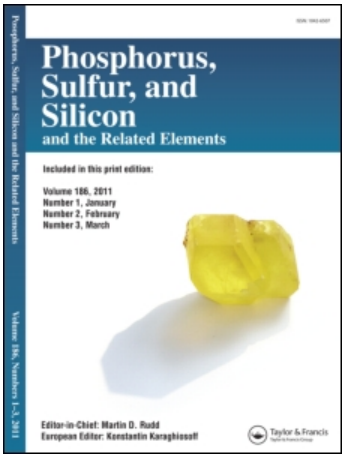


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# Thiaspiroacetals from Carbohydrates

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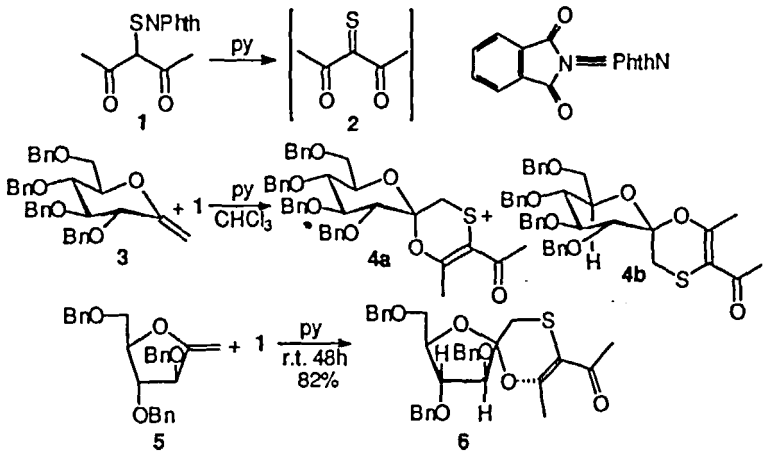
The inverse electron demand [4+2] cycloaddition between glycoexoenitols and α,α'-dioxothiones or *ortho*-thioquinones represents a selective way to achieve 4'-thiaspiroacetals, an unusual class of spiroderivatives, from carbohydrate.

*Keywords:* cycloaddition; spiroacetals

Altohyrtin A-C or lonomycins[1] are representative examples of bioactive natural products characterized by spirosubstructures includeded in the molecule structures. It is evident that the stereoselective formation of the spiro centres is a real challenge for the efficient syntheses of these prominent compounds.

In this paper we describe a new procedure to prepare in a single step, optically pure thiospiroacetals from glycoexoenitols, easily prepared following standard procedures. The phthalimido derivative **1**[2], in the presence of weak bases generates the electron-poor diene **2** which undergoes an inverse electron demand Diels-Alder reaction[2] with *D*-gluco-hept-1-enitol **3**, affording the completely separable 4'-thiaspiroacets **4a** and **4b** in high yield and in a 2.5/1 ratio respectively. (Scheme 1)




SCHEME 1

An extension of this procedure was realised reacting **1** with *D*-arabino-hex-1-enitol **5**. As reported for **3**, the spiroacetal **6** was obtained as single isomer in 82% yield. (Scheme 1) A preliminary investigation of the reactivity of these new compounds was run. Satisfactory results were obtained in the selective transformation of the sugar moiety. Treating the spiroacetals **4** and **6** with acetic anhydride and trimethylsilyltriflate, the selective acetylation of the primary benzyl group on the carbohydrate rings was realised at low temperature (-35 °C) and in 52 and 50% yield respectively.

## *References*

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