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## Phosphorus, Sulfur, and Silicon and the Related Elements

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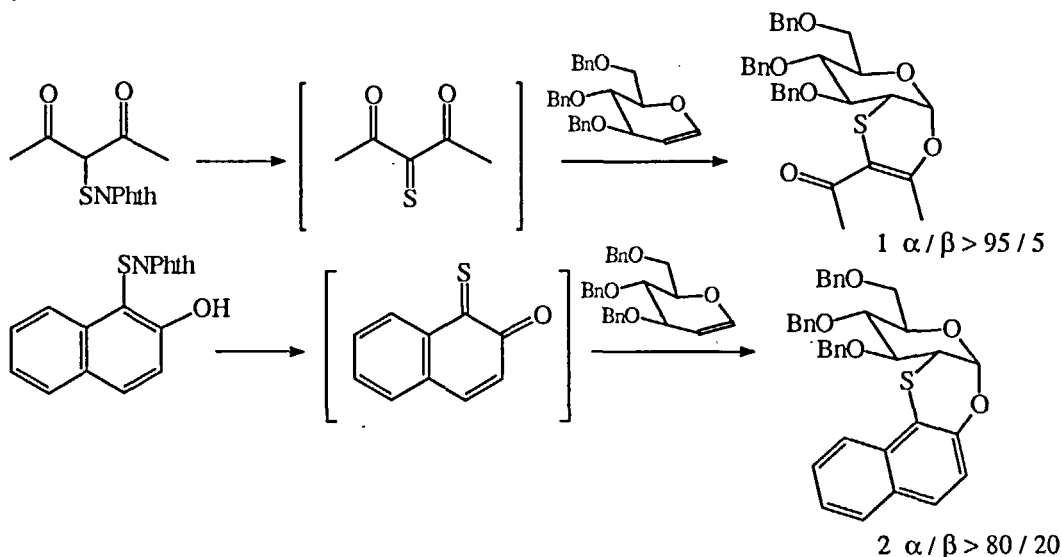
## Sulfur-Mediated Carbohydrate Chemistry: Use of *ortho*-Thioquinones and $\alpha,\alpha'$ -Dioxothiones.

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**Abstract.**  $\alpha$ -O-Glycosides obtained by regio and stereocontrolled [4+2] cycloadditions, are suitable substrates for the stereoselective synthesis of 2-deoxy-O-arylglycosides and  $\beta$ -O-alkylglycosides.

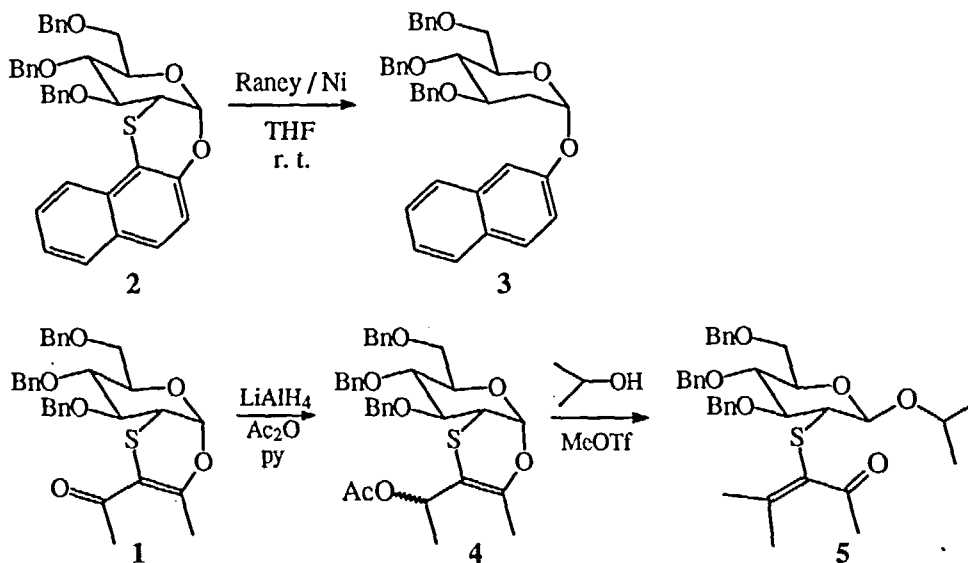
The easy access to alkyl and aryl phthalimidesulfonyl derivatives, synthetic precursors of the highly reactive  $\alpha,\alpha'$ -dioxothiones and *ortho*-thioquinones, allowed the successful use of 1,2-glycals as electron rich dienophiles in inverse electron demand [4+2] cycloadditions<sup>1</sup> (Scheme 1)



Scheme 1

Since the cycloadditions are total regioselective and highly stereoselective the major products formed are  $\alpha$ -O-glycosides<sup>2</sup>.

The potential of the  $\alpha$ -O-glycosyl compounds we prepared is wide; in particular we studied the ring opening of the adducts at carbon 1 and carbon 2 (Scheme 2).



The treatment of cycloadducts **2** ( $\alpha$  isomer) with a suspension of Raney/ Nichel in dry THF at room temperature yielded the 2-deoxy-O-glycoside **3** in 68% yield. It is noteworthy that the formation of 2-deoxy-O-glycosides with this sequence completely avoids the formation of C-glycosides.

Another successful result was achieved in the acid catalysed reactions of **4** with nucleophiles.

The acetyl derivatives **4**, prepared by reduction with  $\text{LiAlH}_4$  of **1** and subsequent protection of the allylic alcohol obtained, revealed to be a suitable substrate for a glycosyl transfer reaction which occurred with the total stereocontrol of the nucleophilic attack. Indeed *isopropyl* alcohol affords the  $\beta$ -O-glycoside **5** as single product. Other oxygen nucleophiles behave similarly, while sulfur or carbon nucleophiles give different results.

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- 2) G. Capozzi, S. Menichetti, C. Nativi, M.C. Simonti, *Tetrahedron Lett.*, **35**, 9451 (1994).