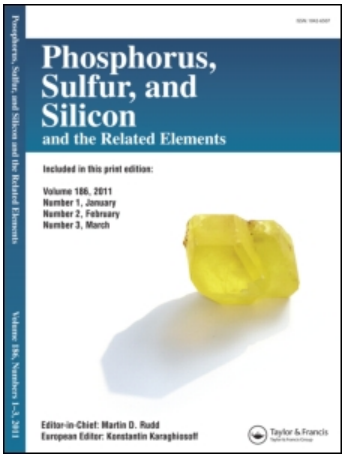

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Regioselective Substitutions of Unsymmetrical 1,2-Diols using Dioxaphospholanes: Applications to Carbohydrates

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Regioselective Substitutions of Unsymmetrical 1,2-Diols using Dioxaphospholanes: Applications to Carbohydrates

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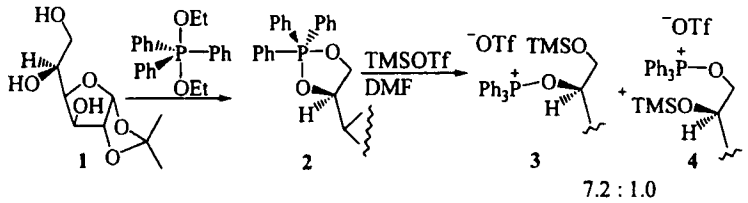
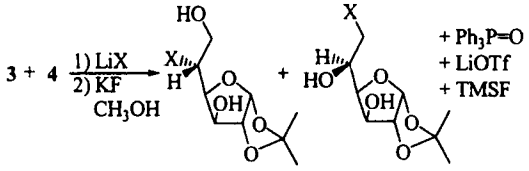
For several years, the method employing 1,3,2λ^5-dioxaphospholanes to effect regioselective substitution of unsymmetrical 1,2-diols has been investigated.[1] As carbohydrates are an abundant source of diols, this study has been extended to the use of 1,2-*O*-isopropylidene-D-glucofuranose **1**. We have synthesized a single dioxaphospholane **2** and subsequently treated it with trimethylsilyltriflate to form oxyphosphonium ions **3** and **4**.



Ions **3** and **4** were then treated with nucleophiles to substitute at the primary or secondary position. Subsequent desilylation was performed by treatment with potassium fluoride.



X	ratios 2°:1°
I	2.4 : 1.0
Cl	3.7 : 1.0
N_3	2.0 : 1.0

Although a majority of secondary product was observed, the drop in regioselectivity from ions **3** and **4** to products was attributed to blocking of the secondary substitution site by the free hydroxyl group. Further studies focus on the role of this hydroxyl group.

References

[1] (a) A.M. Pautard and S.A. Evans, Jr. *J. Org. Chem.*, **53**, 2300 (1988). (b) I. Mathieu-Pelta and S.A. Evans, Jr. *J. Org. Chem.*, **57**, 3409 1992).