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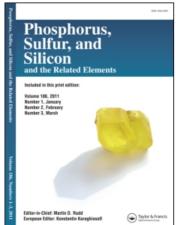
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Regioselective Substitutions of Unsymmetrical 1,2-Diols using Dioxaphospholanes: Applications to Carbohydrates

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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 $1,3,2\lambda^5$ -dioxaphospholanes to effect regioselective substitution of unsymmetrical 1,2-diols has been investigated. 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.

$$3 + 4 \xrightarrow{1) \text{LiX}} \begin{array}{c} \text{HO} & \text{X} \\ \text{HO} & \text{H} \\ \text{OH} \\ \text{CH}_3 \text{OH} \end{array} + \begin{array}{c} \text{HO} & \text{X} \\ \text{HO} & \text{H} \\ \text{OH} \\ \text{OH} \\ \text{OH} \end{array} + \begin{array}{c} \text{H}_{I_{I_{I_{I}}}} & \text{H}_{I_{I_{I_{I}}}} \\ \text{HO} & \text{HO} \\ \text{OH} \\ \text{OH} \\ \text{OH} \\ \text{OH} \\ \text{OH} \\ \text{OH} \end{array} + \begin{array}{c} \text{H}_{I_{I_{I_{I}}}} & \text{H}_{I_{I_{I_{I}}}} \\ \text{HO} & \text{HO} \\ \text{OH} \\ \text{OH} \\ \text{OH} \\ \text{OH} \\ \text{OH} \\ \text{OH} \end{array} + \begin{array}{c} \text{H}_{I_{I_{I_{I}}}} & \text{H}_{I_{I_{I_{I}}}} \\ \text{HO} & \text{HO} \\ \text{OH} \\ \text{$$

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.

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[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).