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Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information: http://www.informaworld.com/smpp/title~content=t713618290

Highly Diastereoselective Synthesis of Anomeric β -O-Glycopyranosyl $\sigma^3 \lambda^3$ -and $\sigma^4 \lambda^5$ -Phosphorus Compounds

Ion Neda^a; Reinhard Schmutzler^a; Ulf Niemeyer^b; Bernhard Kutscher^b; Jürgen Engel^b
^a Institut für Anorganische und Analytische Chemie der Technischen Universität, Braunschweig, Germany ^b ASTA Medica AG, Frankfurt, Germany

To cite this Article Neda, Ion , Schmutzler, Reinhard , Niemeyer, Ulf , Kutscher, Bernhard and Engel, Jürgen(1999) 'Highly Diastereoselective Synthesis of Anomeric β -O-Glycopyranosyl $\sigma^3\lambda^3$ -and $\sigma^4\lambda^5$ -Phosphorus Compounds', Phosphorus, Sulfur, and Silicon and the Related Elements, 147: 1, 279

To link to this Article: DOI: 10.1080/10426509908053620 URL: http://dx.doi.org/10.1080/10426509908053620

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Highly Diastereoselective Synthesis of Anomeric B-O-Glycopyranosyl $\sigma^3\lambda^3$ - and $\sigma^4\lambda^5$ -Phosphorus Compounds

ION NEDA^a, REINHARD SCHMUTZLER^a, ULF NIEMEYER^b, BERNHARD KUTSCHER^b and JÜRGEN ENGEL^b

^aInstitut für Anorganische und Analytische Chemie der Technischen Universität, Postfach 3329, D-38023 Braunschweig, Germany and ^bASTA Medica AG, Weismüllerstr. 45, D-60314 Frankfurt, Germany

A new method for the highly stereoselective synthesis of β -O- $\sigma^3\lambda^3$ and $\sigma^4\lambda^5$ phosphorus-substituted 2,3,4,6-tetrabenzylglucose is presented. The β -diastereoselective synthesis of the carbohydrates containing $\sigma^3\lambda^3$ and $\sigma^4\lambda^5$ phosphorus groups could be accomplished via two main synthetic routes. The first involves the addition of the $\sigma^3\lambda^3$ -phosphorus derivative 3 to the 2,3,4,6-tetrabenzylglucose derivative 1 (α : β = 1:1) in toluene and triethylamine as a catalyst to provide the $\sigma^3\lambda^3$ phosphorus derivative 4 with practically 100% β -diastereoselectivity.

The second route involves the β -stereoselective formation of the $\sigma^3 \lambda^3$ - and $\sigma^4 \lambda^5$ -phosphorus-fluorine derivatives 7 and 8 by the reaction of the β -trimethylsilyl-glycoside 2 with ClPF₂ or P(:O)F₃ in the presence of PF₅ with loss of Me₃SiCl or Me₃SiF. The reaction of 2 with P(:O)F₃ in the absence of PF₅ did not lead to the expected product 8. The use of 4, 7, 8 and other bis(2-chloroethyl)amino-substituted derivatives of phosphorus-containing carbohydrates as glycosyl donors in the glycosylation reaction is discussed.