13th European Carbohydrate Symposium



GLYCOSYLATION WITH TRICHLOROACETIMIDATES IN IONIC LIQUID: A "GREEN" APPROACH TO THE SYNTHESIS OF GLYCOSIDES

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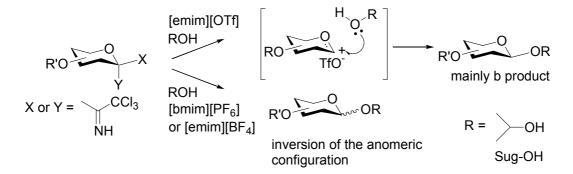
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Ionic liquids (ILs) have recently emerged as a new class of solvents for a wide range of organic reactions.¹ These low melting salts are often referred to as "green solvents", as they are not volatile and can be, in principle, recovered and recycled. The unique characteristics of these reaction media prompted us to investigate their use as solvents in the glycosylation reaction. In fact, the highly polar microenvironment of ILs could affect the course of the reaction through the stabilization of its charged intermediates.

We focussed on the trichloroacetimidate as a suitable activating group due to its wide applicability and effectiveness. Differently protected donors were tested, ranging from disarmed to armed sugars and belonging both to the D- and to the L-series, in order to enlarge the scope of the methodology as widely as possible.² The coupling reactions proceeded under mild conditions and at room temperature and afforded the different glycosydes in fair to excellent yields; in some cases the use of the Lewis acid catalyst was not necessary.

A systematic study describing the behaviour of α and β donors in both coordinating and non-coordinating ILs, strongly supported the hypothesis of the coordination of the oxonium ion by the triflate anion of [emim][OTf], addressing the stereochemical outcome of the glycosylation reaction to the β product. On the other hand, when the reaction was performed in ILs bearing a non-coordinating anion, such as [emim][BF₄] and [bmim][PF₆], the prevailing mechanism leaded to the inversion of the anomeric configuration.

The effectiveness of iterating the same reaction in a recycled solvent was also verified.



[1] (a) Jain, N.; Kumar, A.; Chauhan, S.; Chauhan, S. M. S. *Tetrahedron* **2005**, 1015-1060; (b) Baudequin, C.; Baudoux, J.; Levillain, J.; Cahard, D.; Gaumont, A-C.; Plaquevent, G-C. *Tetrahedron: Asymm.* **2003**, *14*, 3081-3093; (c) Wasserscheid, P. and Welton T., *Ionic Liquid in Synthesis*, Eds.; VCH-Wiley, Weinheim, 2002; (d) Wasserscheid, P.; Keim, W. *Angew. Chem. Int. Ed.* **2000**, *39*, 3772-3789; (e) Welton, T. *Chem. Rev.*

[2] Poletti, L.; Rencurosi, A.; Lay, L.; Russo, G. Synlett 2003, 2297-2300

[3] Rencurosi, A.; Lay, L.; Russo, G.; Poletti, L. submitted.