IP28
Mustard carbonates: the effect of the leaving group

A. S. Aldoshin*, R. Christopher† F. Aricò and P. Tundo
Department of Environmental Science, Informatics and Statistics / Ca' Foscari University of Venice, Italy
†Chemistry Department, University of Dar es Salaam – Tanzania
**Corresponding author: alexander.aldoshin@unive.it*

Keywords: Dialkyl Carbonate, Alkylation; Halogen-free, Neighboring effect, Mustard carbonate anisotropic electrophiles

Abstract

The substitution of a chlorine atom with a carbonate moiety in mustard compounds has led to a new class of molecules, namely mustard carbonates that retain the reactivity of the well-know toxic iprites, but are safe for the operator and the environment [1].
In this work, we report the further development in mustard carbonates chemistry.The influence of the leaving group on the anchimeric effect of sulfur mustard carbonates has been investigated both in autoclave and neat conditions. Results have led to enhanced selectivity of the anchimerically driven alkylation, as well as, to the improved and more accessible reaction conditions [2].
On the basis of the best results obtained the greener and efficient one-pot method of anchimericlly aided alkylation through syntesis of 2-(methylthio)ethyl ethyl carbonate ***in situ*** has been developed.
Besides, a new family of half-mustard carbonate anisotropic electrophiles has been synthesized and their reactivity with aromatic nucleophiles has been investigated.
The selectivity between two possible products deriving from the nucleophilic attack on the anysotropic mustard carbonates has been shown to depend on the intensity of the electron-withdrawig effect (combination of –I and –M effects) of substituent on an aromatic nucleophile in the para-position.

This is remarkable example of how Green Chemistry can domesticate toxic compounds and open the way for their potential application in both preparative and industrial chemistry.

References

[1] a) Q-Q. Wang, R. A. Begum, V. W. Day, K. Bowman-James, *Org. Biomol. Chem.*, **2012**, 10, 8786–8793; b) F. Aricò, M. Chiurato, J. Peltier, P. Tundo, *Eur. J. Org. Chem.* **2012**, 3223-3228; c) F. Aricò, S. Evaristo, P. Tundo, *ACS Sustainable Chem. Eng.* **2013**, 1, 1319-1325; d) F. Aricò, S. Evaristo, P. Tundo. *RSC Adv.* **2014**, 4, 31071-31078.
[2] F. Aricò, A. S. Aldoshin, P. Tundo, *ACS Sustainable Chem. Eng*. **2016**, 4, 2843−2851