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Microwave assisted synthesis of 1,3,5-tris(2-hydroxyethyl)isocyanurate carbamates with C_3 symmetry

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Abstract

Microwave assisted synthesis of 1,3,5-tris(2-hydroxyethyl)isocyanurate carbamates under solventless conditions in short times and good yields is described.

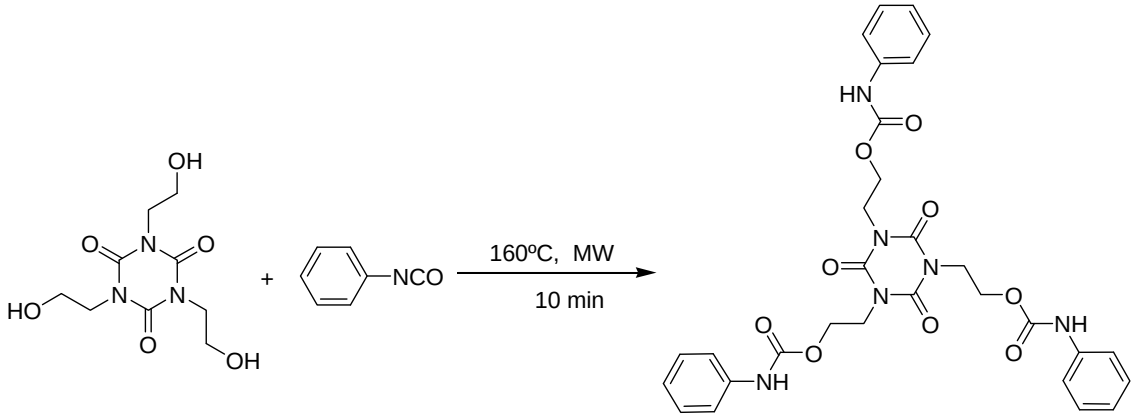
Introduction

The perfunctionalization of polifunctional molecules constitutes an important item in the synthesis of dendrimers.[1] In the field of dendritic structures there has been a report on the use of 1,3,5-tris(2-hydroxyethyl)isocyanurate (THECA) as core for the building of hyperbranched polyesters.[2] An alternative to the ester linkage could be the carbamate group, which presents wider stability towards harsh reaction conditions. In this sense, microwave assisted chemistry is a useful tool in the transformation of functional groups.[3]

Results and discussion

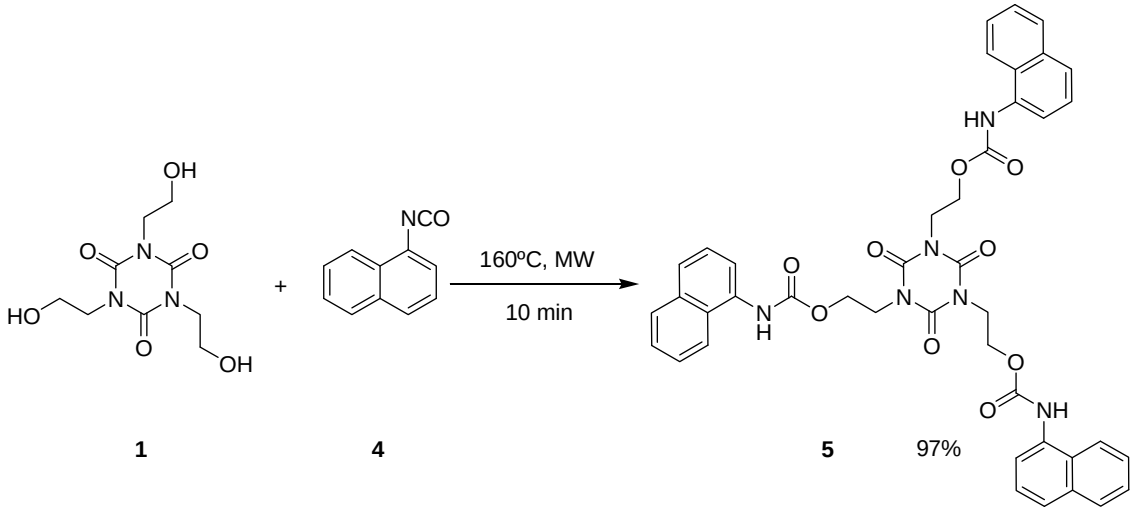
In order to get environmentally friendly reaction conditions we explored reactions in the absence of solvent, which in our previous experience, proved to be suitable for carbamate synthesis.[4] Thus, THECA (**1**) was irradiated in the presence of phenylisocyanate (**2**), 1:3 molar ratio, using a

monomode microwave oven at 160ºC for 10 minutes. The product **3** was obtained in 98% yield. It showed ^{1}H-NMR peaks at δ 4.23 and 4.03 ppm corresponding to -CH_2CH_2- group and at δ 9.27 ppm for the N-H.



1 **2** **3** 98%

The same reaction conditions were optimal for the coupling of α-naphthylisocyanate with THECA, yielding the corresponding tris-naphthylcambamate in 97% yield. Similarly to **3,** this compound showed peaks in the ^{1}H-NMR spectrum at δ 4.11 y 4.31 ppm for -CH_2CH_2- chains and δ 9.16 ppm for N-H.



1 **4** **5** 97%

Representative experimental procedure:

*Synthesis of carbamate **3**.* 1,3,5-Tris(2-hydroxyethyl)isocyanurate (**1**) (0.366 g, 1.40 mmol) and phenylisocyanate (**2**) (0.534 g, 4.2 mmol) were

irradiated in a monomode microwave oven (CEM, Discover) at 160ºC for 10 minutes (power 200W). The crude of reaction was crystallized from acetone yielding the desired carbamate **3** (0.849 g, 98%).

^{1}H-NMR (300 MHz, $CDCl_3$) δ: 9.27 (s, 1H, NHC=O), 7.40 (d, 2H, *J*= 8.20 Hz, ArH), 7.23 (t, 2H, *J*= 7.66 Hz, ArH), 4.26 (t, 2H, *J*= 5.58 Hz, OCH_2), 4.07 (t, 2H, *J*= 5.61 Hz, NCH_2).
^{13}C-NMR (DMSO): 154.0 (NC=O), 149.5 (COO), 139.6 (NHC_{Ar}), 129.2, 123.3, 119.5 (C_{Ar}), 61.5 (OCH_2), 42.4 (NCH_2).
IR (*Golden Gate***):** 3307 (NH), 1687 (C=O), 1598, 1537, 1444, 1313, 1215 (CN), 1062, 754, 690.
MS m/z (%): 619 (M^++1, 5), 618 (M^+, 15), 380 (36), 244(80), 231 (57).

Acknowledgements

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