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Solvent free microwave assisted synthesis of 1,3,5-tris(2-aryloxyethyl)isocyanurates

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Abstract

Synthesis of 1,3,5-tris(2-aryloxyethyl)isocyanurates by esterification of 1,3,5-tris(2-hydroxyethyl)isocyanurate under microwave irradiation in a direct and efficient way in solvent free conditions.

Introduction

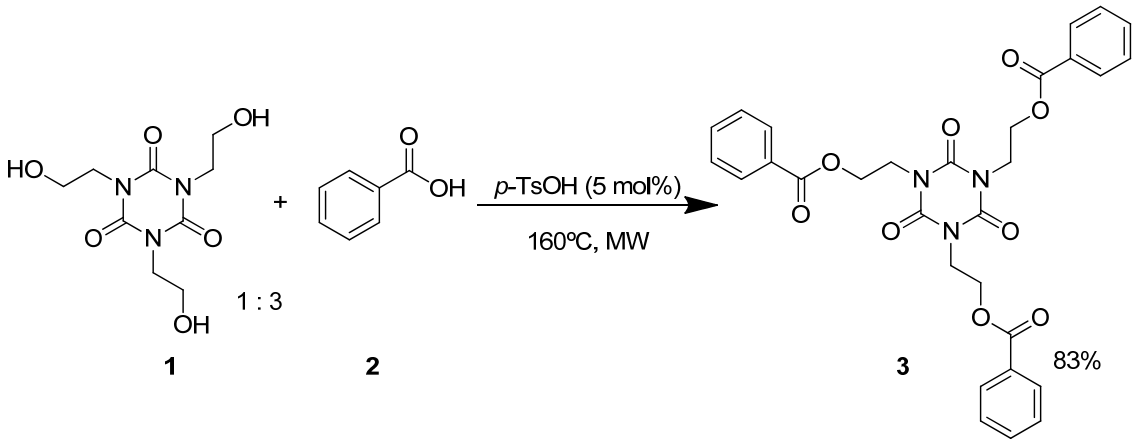
1,3,5-tris(2-hydroxyethyl)isocyanurate (THECA) is a common additive in the preparation of polymers. However its use is not limited to this field. It has been used too in the building up of dendritic structures[1], tripodands,[2] or cage compound. [3] Item in the synthesis of dendrimers the perfunctionalization constitutes an important.[4] In this regard, microwave assisted chemistry is a useful tool in the transformation of functional groups.[5] The C_3 symmetry of THECA esters gives a characteristic shape to this compounds that resembles the Celt symbol triskelion.[6]

Results and discussion

As model reaction, esterification of benzoic acid and THECA were studied. Previously, we had established the suitability of toluene sulphonic acid to catalyze this reaction for aliphatic acids under microwave irradiation.[7]

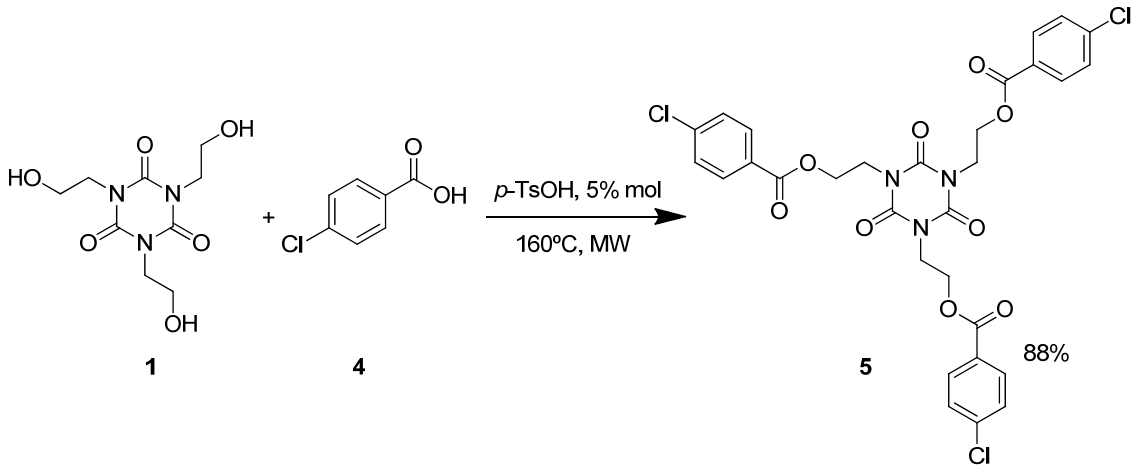
Thus, benzoic acid (**2**) was irradiated in the presence of THECA (**1**) (3:1 molar ratio) in the presence of a 5 mol% of *p*-TsOH, the temperature was set to 160ºC and the irradiation was carried out in an open vessel for 20

minutes (200W power setting). The crude was purified by column chromatography to yield 83% of triester **3** (Scheme 1)**.**



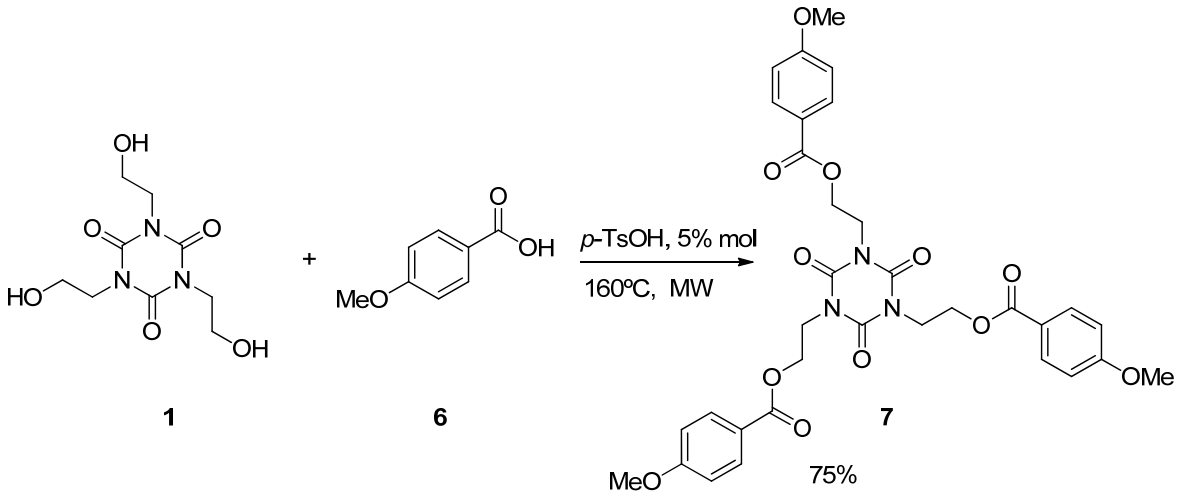
Scheme 1

When, the aromatic ring has a deactivating group as chlorine in *para* position, the ester **5** was obtained in 88% yield after irradiation for 25 minutes at 160ºC (Scheme 2).



Scheme 2

Meanwhile, the esterification with *p*-anisic acid (containing an activating group) took place only in 10 minutes (75% yield of triester **7**, scheme 3).



1 **6** **7**

Scheme 3

General experimental procedure

*Synthesis of triester **3**.* A mixture of 1,3,5-Tris(2-hydroxyethyl)isocyanurate (**1**) (0.150 g, 0.57 mmol), benzoic acid (**2**) (0.534 g, 4.2 mmol) and *p*-TsOH (5.6 mg) were irradiated in a monomode microwave oven (CEM, Discover) at 160ºC for 20 minutes (power 200 W). The crude of reaction was purified through a silica gel column (CH_2Cl_2:MeOH, 9.8:0.2) yielding **3,** as an oil (0.270 g, 83%).

^{1}H-NMR (300 MHz, $CDCl_3$) δ: 8.51 (d, 2H, *J*= 7.07 Hz, ArH), 7.51 (t, 1H, *J*= 7.25 Hz, ArH), 7.38 (d, 2H, *J*= 7.47 Hz, ArH), 4.45 (t, 2H, *J*= 4.84 Hz, OCH_2), 4.26 (t, 2H, *J*= 4.84 Hz, NCH_2).

IR (*Golden Gate***):** 1714 (COO), 1681 (C=O), 1450, 1271, 1114, 1070, 1026, 758, 712.

Acknowledgements

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