

Microwave assisted synthesis of dendrimeric cores

Julio A. Seijas,* M. Ara Carballo-Meilán, Xesús Feás, M. Pilar Vázquez-Tato*

Departamento de Química Orgánica. Facultad de Ciencias. Universidad de Santiago de Compostela. Campus de Lugo. 27002-Lugo. Spain.
julioa.seijas@usc.es, pilar.vazquez.tato@usc.es

Abstract:

Melamine derivatives are synthesized under green conditions, using water as solvent, from anilines and cyanuric chloride in good yields. The prepared tripodal compounds present functionalized aromatic rings that allow former functionalization.

Introduction

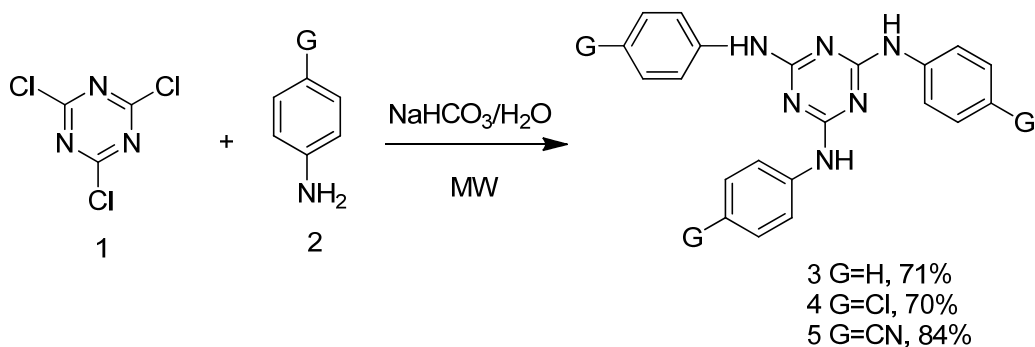
It has been well-known for 60 years that amines react with cyanuric chloride, providing access to amine-functionalized 1,3,5-triazine compounds.¹⁻³ N²,N⁴,N⁶-triaryl-1,3,5-triazine-2,4,6-triamine are of particular interest because many of these compounds are biologically active.⁴⁻⁸ Also, are potentially useful as inexpensive and non-toxic UV-absorbents⁹⁻¹⁰ and pigments.¹¹ Furthermore, they have been used in the building of dendritic polymers, with potential materials applications.¹²

The great development of microwave assisted organic synthesis has also covered the synthesis of melamine derivatives, mostly based in the reaction of cyanuric chloride, in the presence of a base to remove the hydrochloric acid generated and a solvent such as toluene,¹³ dioxane-DMF,⁹ DMSO,¹⁴ it has been also studied under solventless conditions,¹⁵ and as an alternative to basic catalysis the use of acidic YH zeolite in water¹⁶ In this communication we describe the study of the use of a environmentally friendly solvent as water under basic catalysis for the synthesis of melamine derivatives.

Results

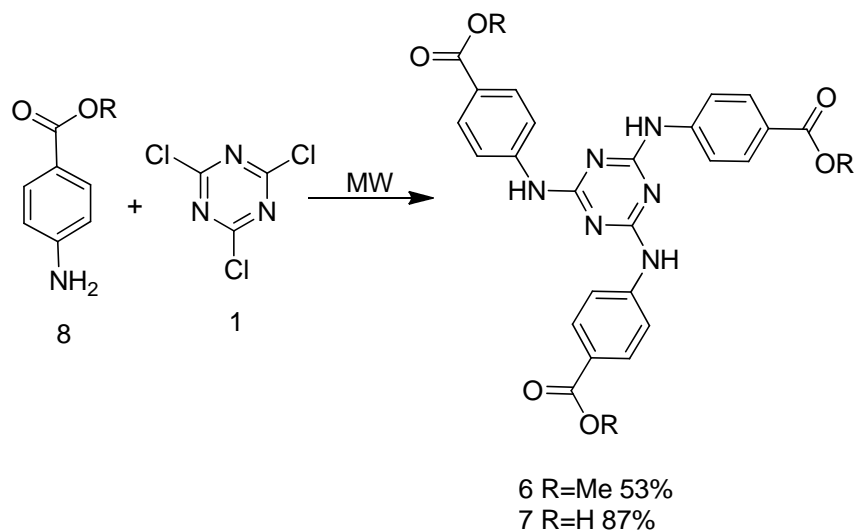
Thus, we studied the reaction of cyanuric chloride with aniline in an aqueous solution of sodium bicarbonate in water irradiated for 3 min in a monomode microwave oven settled with a reflux condenser. This produced a white solid which after purification result in 71% yield of N²,N⁴,N⁶-triphenyl-1,3,5-triazine-2,4,6-triamine (**3**) (Scheme 1). The scope of this reaction was studied so, the above reaction conditions were tested to obtain the N²,N⁴,N⁶-tris (4-chlorophenyl)-1,3,5-triazine-2,4,6-triamine (**4**) from 4-chloroaniline and cyanuric chloride. The irradiation for 3 min. (105°C, 150W) yielded the desired product in 70%. Of special interest is the reaction with 4-aminobenzonitrile because the nitrile group is very versatile and can be converted into acid, amide, amino

or aldehyde groups which can be used to add a second generation. Thus, proceeding as in the previous cases was obtained N^2,N^4,N^6 -tris (4-cyanophenyl) -1,3,5-triazine-2,4,6-triamine (**5**) in very good yield (84%).



Scheme 1

Finally trimethyl 4,4',4''-((1,3,5-triazine-2,4,6-triyl)tris(azanediyl))tribenzoate (**6**) was prepared but, in order to avoid any kind of possible hydrolysis of the ester function the reaction was carried out under solventless conditions. So, methyl 4-aminobenzoate was reacted with cyanuric chloride in the absence of solvent (10 min, 145 ° C, 100W) yielding 52% of triester. However, these reaction conditions using p-aminobenzoic acid instead of the ester led to carbonization of the compound. Meanwhile in aqueous solution it reacted under irradiation with microwaves to give an 87% yield of 4,4',4''-((1,3,5-triazine-2,4,6-triyl)tris(azanediyl))tribenzoic acid (**7**).



Scheme 2

Conclusions

In summary a clean and environmentally friendly method for the synthesis of melamine derivatives by mean of irradiation of anilines an cyanuric chloride in basic media is described.

General Experimental Procedure

A solution of sodium bicarbonate (2.5 g, 0.03 mol) and aniline (2.79 g, 0.03 mol) in 20 mL of water was reacted with cyanuric chloride (1.8 g, 9.76 mol) and irradiated for 2-3 min in a monomode microwave (105°C, 150 W) with a reflux setup. The crude was purified by column chromatography using dichloromethane as eluant. Obtaining compound 3 (2.51 g, 73%) as a white solid.

N²,N⁴,N⁶-triphenyl-1,3,5-triazine-2,4,6-triamine (3)

¹H-NMR (300MHz CDCl₃) δ: 6.97 (s_{broad}, 3H, NH), 7.09 (t, J=7.5Hz, 6H, ArH), 7.33 (t, J= 7.9 Hz, 6H, ArH); 7.58 (d, J=8.6Hz, 6H, ArH). ¹³C-NMR (75MHz, CDCl₃) 121.3, 124.1, 129.0 (C_{Ar}), 138.2 (C_{Ar}-N), 171.5 (N-C_{Ar}-N). MS m/z : (%) 355 (M⁺, 14), 354 (M⁺, 59), 353 (M⁺, 51), 299 (53), 298 (60), 297 (91), 296 (100), 235 (34), 180 (49), 144 (47), 119 (34), 77 (43).IR (KBr): 3404, 1520, 1443, 1228, 757 cm⁻¹

N²,N⁴,N⁶-tris(4-chlorophenyl)-1,3,5-triazine-2,4,6-triamine (4)

¹H-NMR (300MHz, DMSO) δ: 7.17 (dd, J= 8.8 y 38 Hz, 6H, Ar-H); 7.60 (d, J=8.8 Hz, 6H, Ar-H); 9.80 (s, 3H, NH). ¹³C-NMR (75MHz, DMSO) 122.4, 126.9, 128.6 139.1 (C_{Ar}), 164.1 (C-Cl).

4,4',4''-((1,3,5-triazine-2,4,6-triyl)tris(azanediy))tribenzonitrile (5)

¹H-NMR (300MHz, CDCl₃) δ: 7.65-7.69 (m, 6H, ArH); 8.01 (t, J=7.6 Hz, 6H, ArH); 9.91 (s, 3H, NH). MS m/z: (% ES) 313 (17), 285 (20), 103 (14), 101 (100), 81 (14).

trimethyl 4,4',4''-((1,3,5-triazine-2,4,6-triyl)tris(azanediy))tribenzoate (6)

¹H-NMR (300MHz, DMSO) δ: 3.86 (s, 9H, COOCH₃), 7.89 (d, J=9.4 Hz, 6H, ArH), 7.97 (d, J=9.4 Hz, 6H, ArH), 9.79 (s, 3H, NH). MS m/z: (%) 207 (11), 170 (6), 164 (18), 154 (21), 145 (20), 135 (17), 120 (100), 119 (11), 106 (8), 92 (27), 65 (23), 63 (35). IR (KBr): 2951, 1717, 1592, 1413, 1282, 1115, 769 cm⁻¹.

4,4',4''-((1,3,5-triazine-2,4,6-triyl)tris(azanediy))tribenzoic acid (7)

¹H-NMR (300MHz, DMSO) δ: 7.74 (d, J= 9.4 Hz, 6H, ArH), 7.87 (d, J=9.4Hz, 6H, ArH); 10.44 (s, 3H, NH). ¹³C-NMR (75MHz, DMSO) 120.3, 131.0 (C_{Ar}), 142,5 (C-N), 155.1 (N-C-N), 167.6 (CO).MS m/z: (%) 454 (9), 443 (M⁺, 4), 442 (M⁺, 30), 441 (M⁺, 100) IR (KBr): 2953, 1727, 1588, 1545, 1495, 1235, 1175, 768 cm⁻¹

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