



Microwave Assisted Synthesis of Tripodal Tris(1*H*-1,2,3-triazol-4-yl) Cyanurates and Melamines

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Abstract

2,4,6-tris(prop-2-yn-1-yloxy)-1,3,5-triazine and N^2,N^4,N^6 -tri(prop-2-yn-1-yl)-1,3,5-triazine-2,4,6-triamine are used in click reactions to prepare tripodal compounds and dendrimer cores. So, 1,3-cycloaddition with benzyl azide under microwave irradiation afforded each compound, in a 1 minute reaction with good yields.

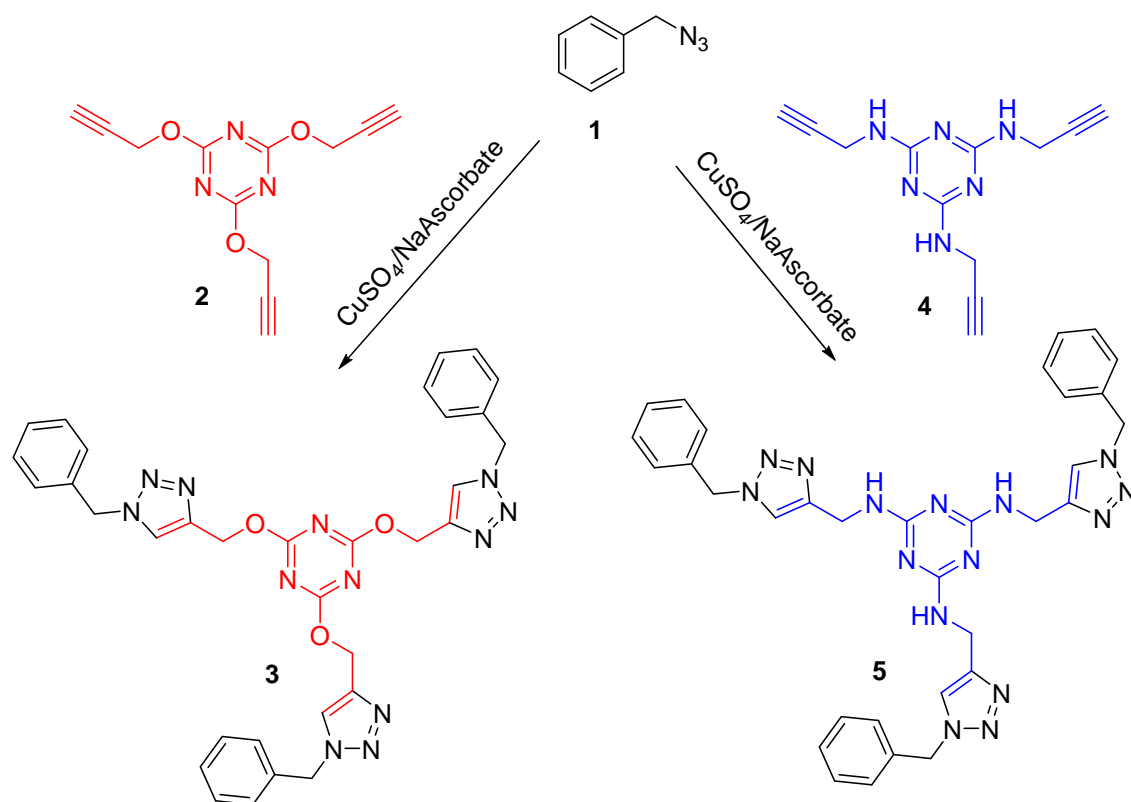
Introduction

Huisgen reaction is a widespread tool in click chemistry,[1] allowing the linkage of two molecular components through a 1,2,3-triazole nucleus. The multiple copper catalysed azide–alkyne Huisgen cycloaddition has been used in the addition of new generations of dendrimer chemistry, generating a real stimulus not only in developing elegant materials of choice, but also in making the leap to industrial scale build-up of dendritic macromolecules.[2] The use of microwaves for enhancing Huisgen reaction has proved to be a useful choice to reduce reaction times and increase yields, however it has not been used as widely as it would be.

Results and discussion

Previously, our group has communicated the synthesis of 2,4,6-tris((1-benzyl-1*H*-1,2,3-triazol-4-yl)methoxy)-1,3,5-triazine (**3**) and N^2,N^4,N^6 -tri(prop-2-yn-1-yl)-1,3,5-triazine-2,4,6-triamine (**5**) from benzylazide and alkynes **2** or **4**, in 46 and 97% yields respectively. The reaction was carried out at room temperature and required a reaction time of 24 hours (Scheme 1).[3]

In this communication we study the preparation of these suitable compounds by irradiation with microwaves. Although several solvents and temperatures were tried, the optimal results were obtained for THF-water at 100°C for 1 minute. The yield for compound **3** was indeed increased, about 20%, meanwhile for compound **5**, whose yield already was very good, remained almost unchanged (Table 1). But a dramatic reduction in reaction time was observed in both cases, being the more important advantage of the procedure developed. Also it is noteworthy that the change of DMF for THF makes the work up of the reaction easier.



Scheme 1

Table 1

Compound	Solvent	Temperature	Reaction Time	Yield(%)
3	DMF-water	rt	1 day	46
5	DMF-water	rt	1 day	97
3	THF-water	100°C-MW	1 minute	68
5	THF-water	100°C-MW	1 minute	91

Conclusions

We have improved the straightforward method to synthesize 1H-1,2,3-triazoles with C_3 symmetry derived of trispropargyl cyanurate or melamine by Huisgen reaction that had been developed in our group. The irradiation with microwaves implies a remarkable reduction in reaction times and, sometimes, an increase in the yield. This made the method very promising to apply to the synthesis of dendrimers since the triazole linker has proven to be resistant under acidic or nucleophilic sol-gel conditions.

Experimental procedure

In a vessel were introduced the alkyne (1 mmol), benzyl azide (3.5 mmol), THF (1 mL) and distilled water (1 mL). This mixture was sonicated and sodium ascorbate (0.5 mmol) and copper sulphate (0.05 mmol) were added. The vessel, with a magnetic stirring bar, was sealed and irradiated for 1 minute at 100°C (100 W, CEM-Discover). The precipitate was filtered off and washed with cold methanol. The organic phase was evaporated and the residue chromatographed through a silica gel column.

Acknowledgements

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References

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