

Área: ORG

## New methodology for the synthesis of the tris-[1,2,4]triazolo-[1,3,5]-triazine core from acylhydrazides

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Palavras Chave: Heterocycle, Tristriazolotriazine, Organic Synthesis, Triazine, Acylhydrazides.

### Highlights

A new synthetic route to tris-[1,2,4]-triazolo-[1,3,5]-triazine using acylhydrazides enables efficient access to functionalized TTT derivatives.

### Abstract

The tris-[1,2,4]-triazolo-[1,3,5]-triazine (TTT) core is composed of three 1,2,4-triazole heterocyclic units condensed onto a 1,3,5-triazine, resulting in a planar structure with a high nitrogen content. Since the first report of a phenyl-TTT derivative, in 1961 by Huisgen [1], TTT derivatives have attracted considerable attention due to their promising applicability in liquid crystals [2,3] and luminescent materials [4]. Up to the present moment, TTTs are obtained from the reaction between cyanuric chloride and a tetrazole derivative [1–4], whose formation is limited and involves the use of azide, a hazardous reagent. Therefore, the development of new methodologies is crucial for expanding the library of TTT-derived molecules. In the search for a new synthetic methodology, it was found that replacing tetrazoles with hydrazides could lead to the formation of an intermediate similar to that obtained in the traditional route. Thus, in the present work, we report the use of hydrazides (1) in the synthesis of a substituted phenyl TTT derivative (4-OMe) (3). Various methodological modifications were tested, including different solvents, bases, dehydrating agents, temperatures, and reaction times. The most efficient reaction so far employed three equivalents of 4-methoxybenzohydrazide (1), one equivalent of cyanuric chloride (2), six equivalents of pyridine, and an excess of thionyl chloride in acetonitrile, yielding exclusively the tangential TTT isomer (3) in 72% yield after purification by column chromatography. Compound 3 was characterized by its melting point, FTIR and NMR spectroscopy. We are currently broadening the scope of this methodology by employing hydrazides derived from pyridine, acetohydrazide, and hydrazides bearing various substituents (2-OMe, 3-OMe, 4-OMe, 3,4,5-OMe, 4-tert-butyl, 4-NO<sub>2</sub>, 3-NO<sub>2</sub>), thereby further validating the efficiency of the methodology.

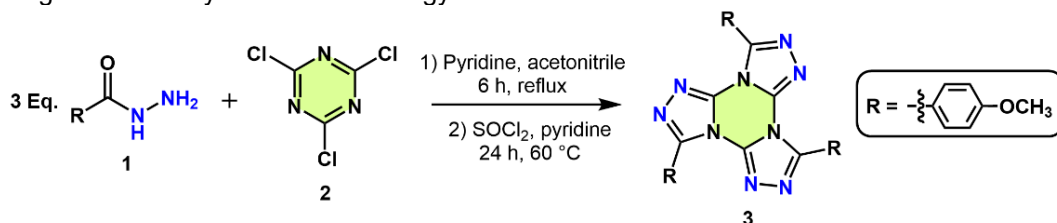


Figure 1. Representation of the newly developed methodology for the synthesis of TTTs from acylhydrazides.

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