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## Synthesis of New $1\lambda^4$ -[1,2,4,6]Thiatriazines

ANDRÉ D. STOLLER\*

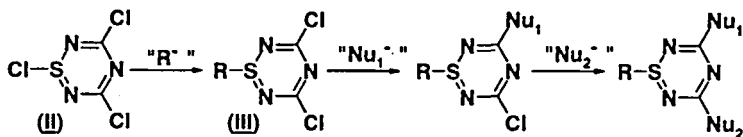
Novartis Crop Protection AG, WRO-1060.2.40, CH-4002 Basel, Switzerland

A very short, effective and widely applicable synthesis of substituted 1-carbo- $1\lambda^4$ -[1,2,4,6]-thiatriazines is presented. The first step consisting of replacing the chlorine atom at the sulfur of trichlorothiatriazine by a carbon atom is described for the first time.

**Keywords:** thiatriazine;  $1\lambda^4$ -[1,2,4,6]-thiatriazine; trichlorothiatriazine

$1\lambda^4$ -[1,2,4,6]-Thiatriazines are seldom encountered in the chemical literature. The corresponding trichlorothiatriazine **II** has been known for over 20 years<sup>(1)</sup> but didn't find application despite of its convenient preparation and huge synthetic potential.

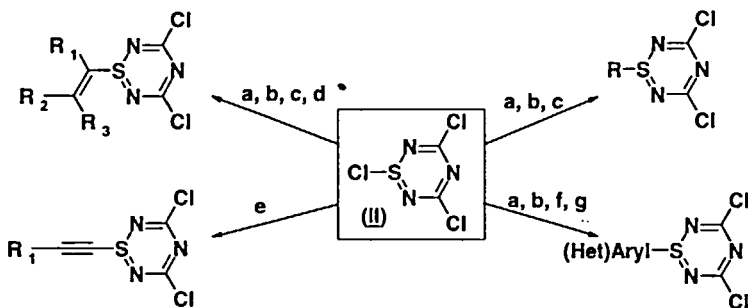
This communication deals with a novel synthetic approach to substituted 1-carbo- $1\lambda^4$ -[1,2,4,6]-thiatriazines of type **I**<sup>(2)</sup> using **II** as starting material and central building block (scheme 1). The three chlorine atoms of **II** are successively substituted by the corresponding nucleophiles. The position at the sulfur is the most electrophilic one.



SCHEME 1 Synthesis of substituted  $1\lambda^4$ -[1,2,4,6]-thiatriazines.

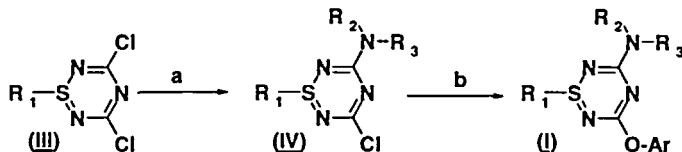
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Synthetic methods with general applicability allowing the introduction of various types of substituents (alkyl,  $\alpha$ -alkenyl,  $\alpha$ -alkinyl, aryl and heteroaryl) at the 1-position of the heterocycle are described. These methods mostly rely on organometallic chemistry (scheme 2).



SCHEME 2 a) Organo-ZnX, b) (Organo)<sub>2</sub>AlCl, c) Organo-Zr(Cl) (Cp)<sub>2</sub>, d) Nucleophilic alkene / Lewis acid cat., e) Lithium tetraalkynylalane, f) Friedel-Crafts reaction, g) Organo-SiR<sub>3</sub> or organo-SnR<sub>3</sub> / Lewis acid catalysis.

The resulting dichlorothiatriazines **III** react with amines to the corresponding amino-derivatives **IV** which are converted to compounds **I** by treatment with a phenolate in presence of trimethylamine (scheme 3).



SCHEME 3 a) HN(R<sub>1</sub>)(R<sub>2</sub>) / THF / 0°-25°C, (85-99%), b) ArOH, NaOH, Me<sub>3</sub>N, H<sub>2</sub>O/CH<sub>2</sub>Cl<sub>2</sub> / 25°C, (80-99%).

## References

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- [2] Patents: Ciba-Geigy A.G. WO 9601814-A1 (1994.07.07), Novartis A.G. WO 9725319-A1 (1996.01.05), WO 9808845-A1 (1996.08.27).