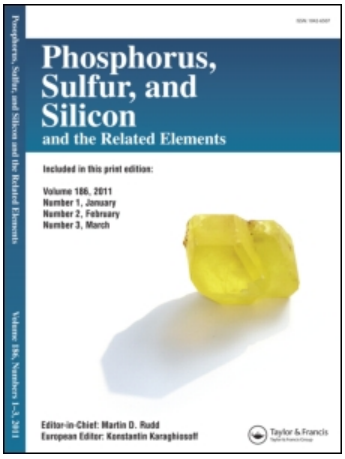

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Synthesis of New $1\lambda^4$-[1,2,4,6]Thiatriazines

ANDRÉ D. STOLLER*

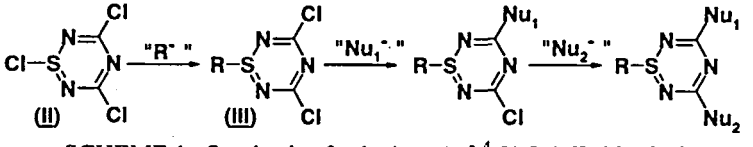
Novartis Crop Protection AG, WRO-1060.2.40, CH-4002 Basel, Switzerland

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[1] but didn't find application despite of its convenient preparation and huge synthetic potential.

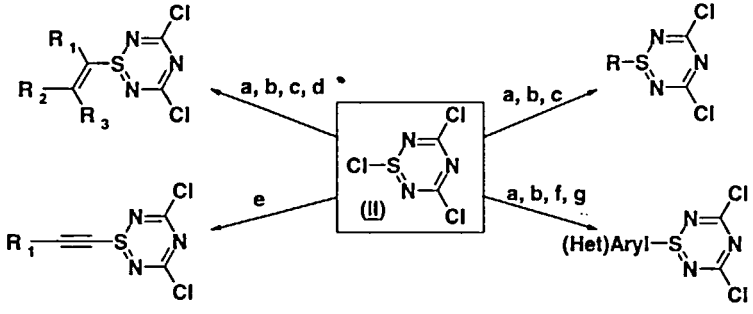
This communication deals with a novel synthetic approach to substituted 1-carbo-$1\lambda^4$-[1,2,4,6]-thiatriazines of type **I** [2] using **II** as starting material and central building block (scheme 1). The three chlorine atoms of **II** are successively substituted by the corresponding nucleophiles.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



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

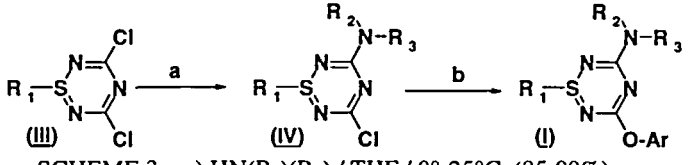
* e-mail: andre.stoller@cp. novartis.com

Synthetic methods with general applicability allowing the introduction of various types of substituents (alkyl, α-alkenyl, α-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) $(Organo)_2AlCl$, c) Organo-Zr(Cl) $(Cp)_2$, d) Nucleophilic alkene / Lewis acid cat., e) Lithium tetraalkinylalanate, f) Friedel-Crafts reaction, g) Organo-SiR_3 or organo-SnR_3 / 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) $HN(R_1)(R_2)$ / THF / 0°-25°C, (85-99%), b) ArOH, NaOH, Me_3N, H_2O/CH_2Cl_2 / 25°C, (80-99%).

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[1] G. Voss, E. Fischer, G. Rembarz and W. Schramm, Z. *Chem.* 16(12), 490–491 (1976).
[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).