

**XXI INTERNATIONAL SYMPOSIUM
„ADVANCES IN THE CHEMISTRY OF
HETEROORGANIC COMPOUNDS”**



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**Section
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“Advances in the Chemistry of Heteroorganic Compounds”

is dedicated to

Professor
Tadeusz Gajda

and

Professor
Janusz Zakrzewski

on the occasion of their 70th birthday

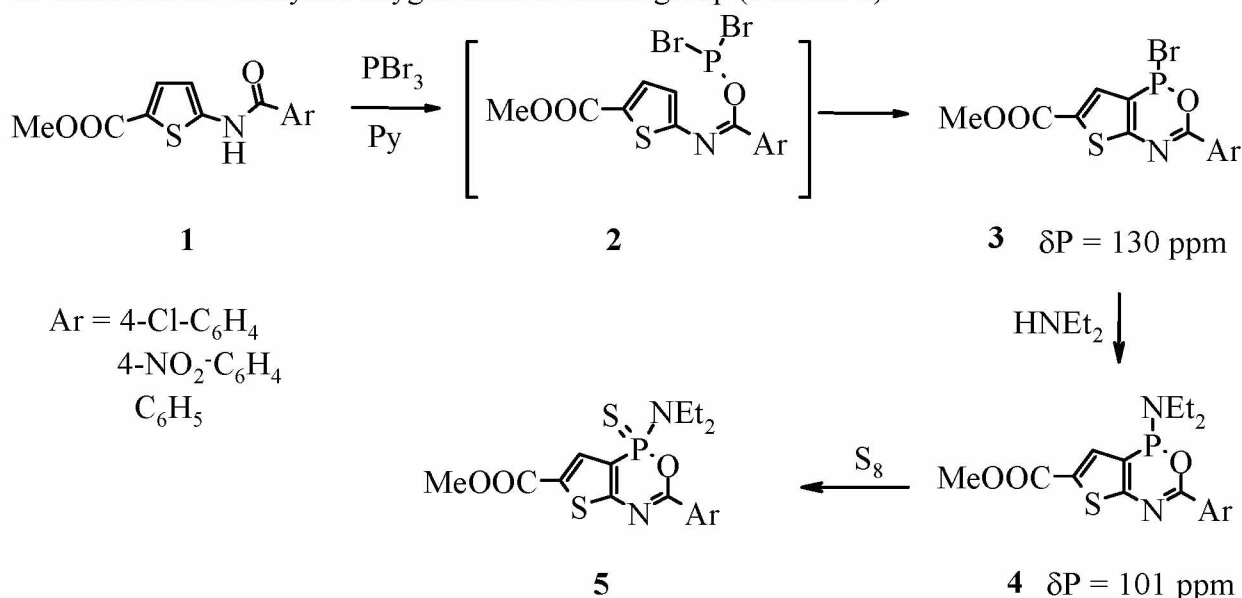


Synthesis of 1,2-dihydrothieno-1 λ^5 -[2,4,1]oxazaphosphine

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Carboxylic acid amides known to be functionally active with respect to phosphorus (III) halides [1-4]. N-acylated 2-aminothiophene derivatives **1**, containing an exocyclic O-nucleophilic atom in its structure, are phosphorylated with phosphorus(III) bromide to form a bicyclic system containing phosphorus atom, namely, dihydrothieno[2,4,1]oxazaphosphine **3**. The reaction proceeds with the participation of two centers, namely, the endocyclic thiophene C3-atom and the exocyclic oxygen atom of amide group (Scheme 1).



Scheme 1. Phosphorylation of N-acylated 2-aminothiophene derivatives with phosphorus(III) bromide.

Due to the higher nucleophilic reactivity of O-atom of the exogroup compared to the sp^2 -hybridized C-center, perhaps, phosphorylation of compound **1** begins from the O-center of the amide group. As a result, an intermediate acyclic structure **2** is formed. The subsequent intramolecular interaction between functional group PBr_2 and C nucleophilic center in the third position of the thiophene ring proceeds to form an energetically favorable six-membered cyclic structure, containing endocyclic P atom, namely, [2,4,1] oxazaphosphine. Three- and four-coordinated phosphorus derivatives **4**, **5** were synthesized on the basis of bromoanhydride **3** formed.

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