Synthesis and structural investigation of *N*-acyl selenophosphoramides†

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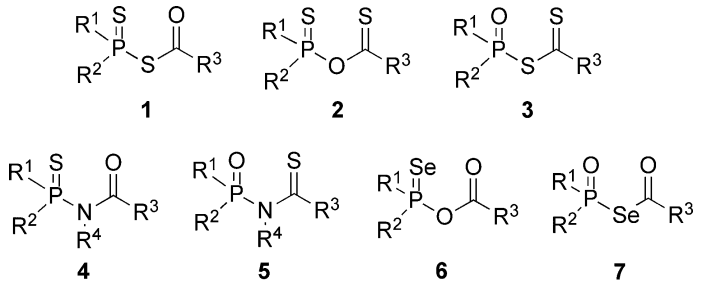
2-Amino-2-seleno-5,5-dimethyl-1,3,2-dioxaphosphorinane reacts with acyl chlorides (4-chlorobenzoyl chloride or pivaloyl chloride) yielding the respective *N*-acyl selenophosphoramides. These derivatives do not isomerise to the related selenocarbonyl imides. X-ray study of *N*-(4-chlorobenzoyl)-2-amino-2-seleno-5,5-dimethyl-1,3,2-dioxaphosphorinane indicates that the selenium atom is placed in the equatorial position. The next compound studied, *N*-pivaloyl-2-amino-2-seleno-5,5-dimethyl-1,3,2-dioxaphosphorinane, crystallises with both axial/equatorial conformers present in the asymmetric unit. Finally, 2-amino-2-seleno-5,5-dimethyl-1,3,2-dioxaphosphorinane is present in the solid state in the form with the selenium atom in the axial position. The results are presented together with X-ray structures of previously synthesised and described cyclic *O*-acyl monoselenophosphates.

Introduction

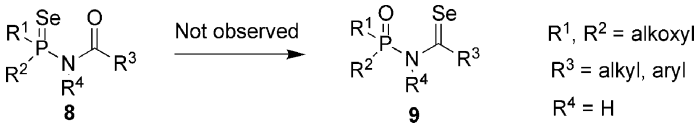
Selenium compounds play an important role in biological processes, and their synthesis has been intensively studied.[1] The sulfur analogues of acyl selenophosphates *S*-acyl dithiophosphates **1**[2,3] and *N*-acyl thiophosphoramides **4**[4–6] are not stable and isomerise to the respective thiocarbonyl derivatives **2**, **3** and **5** (Scheme 1). As a result, they can be used as an efficient and chemoselective thioacylating agents. The influence of substituents $R^1$and R^2 at the phosphorus atom, R^3 at the acyl carbon and R^4 at the nitrogen atom on isomerisation was investigated, but the mechanism of this process has not been elucidated so far. It was established, however, that the presence of alkoxyl groups R^1, R^2 and an alkyl or aryl group R^4 is necessary for isomerisation.[2,6]



Scheme 1

Recently, we synthesized *O*-acyl monoselephosphates **6** in the reaction of the respective monoselenophosphoric acid salts >P(Se)O$^-$ with acyl chlorides. Some of these compounds isomerise to *Se*-acyl derivatives **7** (Scheme 1). All the collected experimental data indicate that this process has a radical mechanism.[7]

In this paper we present a synthesis of *N*-acyl selenophosphoramides **8** together with their X-ray structures, and we discuss their tendency to isomerise. The isomerisation of imides **8** to **9** (Scheme 2) could give selenoacylating agents, analogous to sulfur derivatives **1** and **4**. The X-ray structures of **8** were compared with those obtained for *O*-acyl monoselenophosphates **6**.



Scheme 2

Results and discussion

For our investigations we chose derivatives of 2-seleno-5,5-dimethyl-1,3,2-dioxaphosphorinane. These turned out to be stable and crystalline,[2] as is crucial for X-ray studies. The related *S*-acyl dithiophosphates **1** and *O*-acyl monoselenophosphates **6** with the same R^1 and R^2 groups are known to have a high tendency to isomerise.[2,7]

N-acyl selenophosphoramides **8a** and **8b** were prepared *via* reaction of selenophosphoric acid amide **11a** with acyl chlorides **12a,b** (Scheme 3).

The starting material for selenophosphoric acid amides was 2-chloro-5,5-dimethyl-1,3,2-dioxaphosphorinane **10**.[8] 2-Amino-2-seleno-5,5-dimethyl-1,3,2-dioxaphosphorinane **11a** was obtained by addition of **10** to liquid ammonia followed by selenization. In the case of 2-phenylamino-2-seleno-5,5-dimethyl-1,3,2-dioxaphosphorinane **11b**, **10** was treated with aniline according to the procedure described by Stec and Zielinska *et al.*[9] 2-Methylamino-2-seleno-5,5-dimethyl-1,3,2-dioxaphosphorinane **11c** was synthesized by the reaction of 2-chloro-2-seleno-5,5-dimethyl-1,3,2-dioxaphosphorinane (obtained by heating **10** with selenium in toluene)[10] with a methanolic solution of methylamine.

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† Electronic supplementary information (ESI) available: X-ray data, Figs. S1–S3, and NMR spectra. CCDC reference numbers CCDC 717028 (**6c**), 717029 (**6d**), 717030 (**6e**), 717031 (**8a**), 717032 (**8b**) and 717033 (**11a**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b907641g