Reactions of 2-nitrosoanilines with trivalent phosphorus compounds and application of the products of these transformations in the synthesis of nitrogen heterocycles

MSc Emilia Łukasik

supervisor: Assoc. Prof. Zbigniew Wróbel

Searching for a new and effective ways of synthesis of nitrogen heterocycles is an important goal for chemists, because these compounds occur as a core in the structures of many biologically active substances.

The aim of my studies was the synthesis of (2-arylamino)aryliminophosphoranes and their applications, as starting materials, in the synthesis of nitrogen heterocyclic systems.

At the first stage of my research I have established a method for the synthesis of (2-arylamino)aryliminophosphoranes, starting from the *N*-aryl-2-nitrosoanilines and trivalent phosphorus compounds. The best results were received by using a triphenylphosphine. Using harsher reaction conditions and an excess of triphenylphosphine, acting at the beginning as the reducing agent, also allowed to obtain desirable iminophosphoranes, starting from 2-nitro-diarylamines. This method has enabled the synthesis of such iminophosphoranes, for which the starting 2-nitrosodiarylamines are impossible to be obtained by nucleophilic substitution of hydrogen.

The next goal was the application of (2-arylamino)aryliminophosphoranes for the synthesis of the fused heterocyclic systems. I have developed some new methods for the synthesis of 1-arylbenzimidazoles, as far as possible, previously obtained (2-arylamino)-aryliminophosphoranes. I have obtained 1-aryl-2-aminobenzimidazoles, 1-arylbenzimi-dazoles, 1-arylbenzimidazole-2-thiones and 1-aryl-2-benzimidazolones carrying out the reactions of these compounds with isocyanates, acid chlorides, CS_2 and CO_2, respectively. The latter group of products include compounds with known biological activity. The benzimidazole derivatives were also formed by the reaction of (2-arylamino)-aryliminophosphoranes with the Vilsmeier reagent. When I had used *N*-alkyl derivatives of (2-arylamino)aryliminophosphoranes in this reaction, than I received dibenzodiazepine derivatives. Reactions with sodium nitrite led to benzotriazole derivatives. The quaternization of (2-arylamino)aryliminophosphoranes and *N*-alkyl (including *N*-allyl) derivatives, provided to selectively substituted 2-aminodiarylamine derivatives. This type of the diallylic

compounds were used for the synthesis of benzodiazocine derivatives by using the ring closing metathesis in order to obtain the eight-membered heterocycles.

(2-Arylamino)aryliminophosphoranes have been proved to be readily available and convenient intermediates in the synthesis of the fused nitrogen heterocycles. Thus, it enables to replace arylenediamine derivatives, which sometimes are more difficult to obtain and less stable.