

## Synthesis and $^1\text{H}$ - $^1\text{H}$ spectroscopy NOESY studies of (*E*)-(2-chloro-2-phenylvinyl)diaminophosphine oxide

*Lobova A.M.*<sup>1</sup>, *Egorova A.V.*<sup>2</sup>, *Egorov D.M.*<sup>1</sup>, *Baichurin R.I.*<sup>3</sup>

<sup>1</sup> St. Petersburg State Institute of Technology (Technical University), St. Petersburg, Russia

<sup>2</sup> St. Petersburg Federal Research Center of the Russian Academy of Sciences, St. Petersburg, Russia

<sup>3</sup> Herzen State Pedagogical University of Russia, St. Petersburg, Russia

E-mail: diekerze54@gmail.com

### Introduction

As sure as a two of the most useful methods for determination and confirmation structures of compounds are – X-ray diffraction and the NMR spectroscopy. The benefit of the second method is the possibility to carried out in solutions and in the crystalline state. Also NMR is giving possibilities for studding the weak magnetic interactions.

### Results and Discussion

Here we investigate the reaction between secondary aliphatic amines and  $\beta$ -chlorophenylvinylphosphonic acid dichloride (Fig. 1).

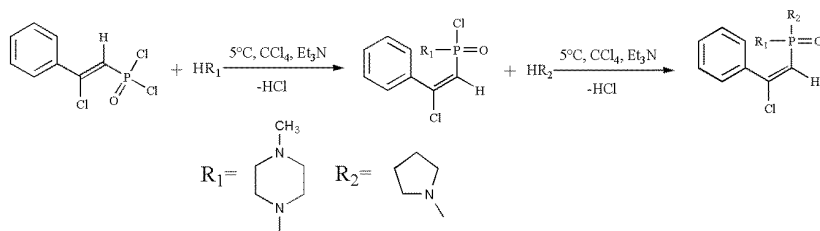


Figure 1. Scheme for the synthesis of (*E*)-(2-chloro-2-phenylvinyl)diaminophosphine oxide

Previously, using two-dimensional  $^1\text{H}$ - $^1\text{H}$  NOESY spectroscopy, it was proven that in the reaction of  $\beta$ -chlorophenylvinylphosphonic acid dichloride with various aliphatic alcohols, *Z*-isomers of *O*-functionalized phosphonates are selectively formed [1]. Thus, in the  $^1\text{H}$ - $^1\text{H}$  NOESY spectrum of di(prop-2-yl) [(*Z*)-2-chloro-2-phenylethenyl]-phosphonate, there is nuclear Overhauser effect between the *ortho*-proton of the aromatic ring and the =CH moiety (Fig. 2). For the *E*-isomer, such effect is not possible.

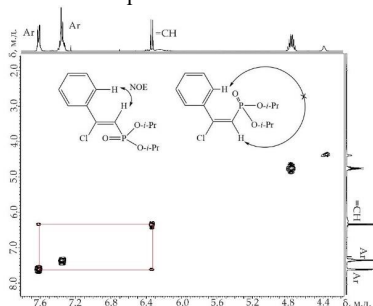


Figure 2.  $^1\text{H}$ - $^1\text{H}$  NOESY di(prop-2-yl) [(*Z*)-2-chloro-2-phenylethenyl]-phosphonate

We assumed that the reaction of aliphatic amines with  $\beta$ -chlorophenylvinylphosphonic acid dichloride would proceed with the formation of products of a similar structure. But in contrast, the synthesis of substituted diaminephosphine oxide is characterized by the formation of the *E*-isomer, as evidenced by the absence of a cross-peak between the proton of the vinyl bond and the proton of the phenyl ring, as in Fig. 2. However, the initially selected parameters with a mixing time of 0.5 sec did not allow us to accurately establish the correlation of signals between the vinyl fragment and the protons of secondary amines. When the mixing time was increased to 1 sec, a cross-peak of the proton of the vinyl bond and the multiplet corresponding to the proton of the pyrrolidine ring closest to the phosphorus atom could be observed in the  $^1\text{H} - ^1\text{H}$  NOESY spectrum (Fig. 3).

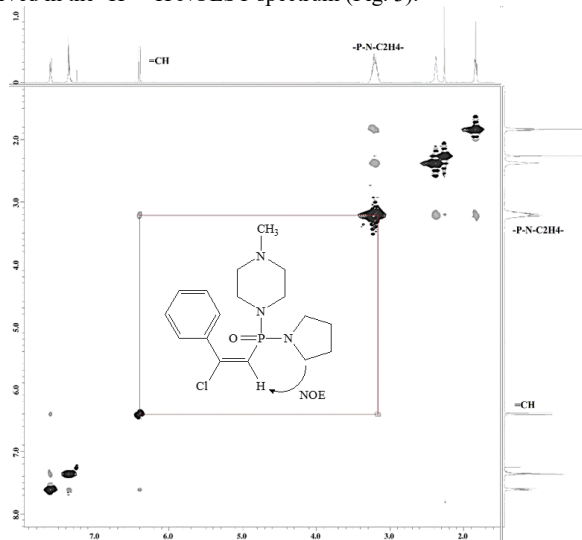


Figure 3.  $^1\text{H} - ^1\text{H}$  NOESY of (*E*)-(2-chloro-2-phenylvinyl)diaminophosphine oxide

This ratio of cross-peaks indicates that the primary attack by a secondary aliphatic amine on the acid chloride molecule of  $\beta$ -chlorophenylvinylphosphonic acid occurs at the chlorine atom located closer to the double bond.

The use of two-dimensional  $^1\text{H} - ^1\text{H}$  spectroscopy NOESY has proven itself as a method for monitoring the structure of the resulting phosphonate. In the course of further research, it will be used to establish at what point isomerization occurs; monitoring on the  $^{31}\text{P}$  nucleus will perhaps make it possible to understand through which intermediate structures the reaction proceeds.

## Acknowledgements

This study was supported by within the state assignment of Ministry of Education and Science of the Russian Federation for 2022-2024 (No. 122041100086-5).

## References

1. A. V. Egorova, D. M. Egorov, N. O. Sonin, I. E. Kolesnikov, D. V. Pankin, A. A. Manshina, R. I. Baichurin, – *Russ. J. Gen. Chem*, 92, 92, 2191–2196 (2022).