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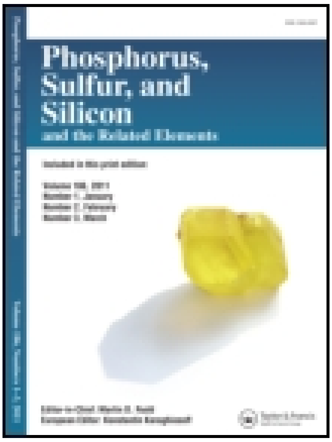

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Synthesis and Crystal Structure of 2-Substituted 3-Aryl-2-Oxophenylbenzo[E]-1,4,2-Oxazaphosphinanes

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Published online: 01 Jul 2015.

To cite this article: Mudaris Dimukhametov, Natalya Belova, Vladimir Mironov, Ekaterina Mironova, Dmitry Krivolapov, Petro Onys'ko & Yulia Rassukanaya (2015) Synthesis and Crystal Structure of 2-Substituted 3-Aryl-2-Oxophenylbenzo[E]-1,4,2-Oxazaphosphinanes, Phosphorus, Sulfur, and Silicon and the Related Elements, 190:5-6, 943-946, DOI: 10.1080/10426507.2014.993756

To link to this article: http://dx.doi.org/10.1080/10426507.2014.993756

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Phosphorus, Sulfur, and Silicon, 190:943–946, 2015
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ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426507.2014.993756

SYNTHESIS AND CRYSTAL STRUCTURE OF 2-SUBSTITUTED 3-ARYL-2-OXOPHENYLBENZO[*E*]-1,4,2-OXAZAPHOSPHINANES

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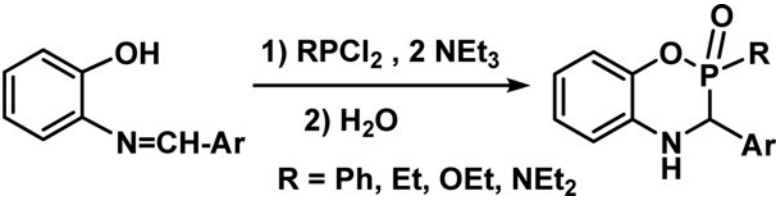
GRAPHICAL ABSTRACT



Abstract *Stereoisomers of 2-substituted 3-aryl-2-oxobenzo[e]-1,4,2-oxazaphosphinane derivatives were obtained by the phosphorylation of 2-arylideneaminophenols with dichlorophenylphosphine in the presence of triethylamine followed by the water treatment, which were isolated by column chromatography as pure diastereoisomers. Their structure was determined by NMR and XRD.*

Keywords Aminophosphinic acid; oxazaphosphinane; intramolecular Pudovik reaction; diastereoisomer; crystal structure; conformation

Among aminophosphinic acid derivatives, cyclic benzo[*e*]-1,4,2-oxazaphosphinanes are studied the least, only several works[1] are devoted to the synthesis and properties of some of their representatives. These compounds, as well as their aminophosphonic analogs, are of interest from the point of view of their biological activity[2]. In the present work, we suggest a new convenient approach to the preparation of aminophosphinic acid derivatives, *viz.*, 3-aryl-2-R-2-oxobenzo[*e*]-1,4,2-oxazaphosphinanes (**1**), based on the stepwise one-pot reaction of the equimolar amounts of 2-arylideneaminophenols (**2**) with $RPCl_2$ and water in the presence of NEt_3. The process is likely to include the intermediate formation of hydrophosphoryl compounds (**3**) (Scheme 1), which, however, were not detected by

Received 19 August 2014; accepted 23 November 2014.

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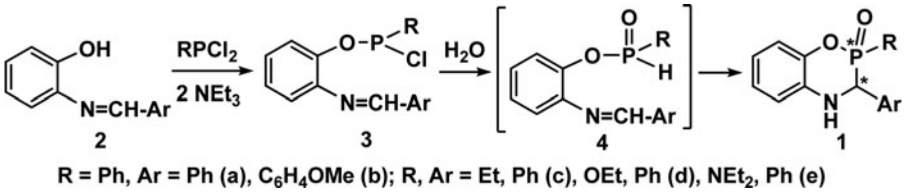
NMR because of their very fast conversion to the final cyclic products (**1**) through the intramolecular Pudovik reaction (intermediate **4**).



Scheme 1

Compounds (**1**) are formed as mixtures of diastereoisomers (d_1, d_2) in the ratio $(d_1) : (d_2) = 3 : 1$ (**1a**) and $(d_1) : (d_2) = 2 : 1$ (**1b–e**).

The diastereoisomers (**1a**,**b**) were isolated by column chromatography **3**. Their structures were confirmed by XRD (Figures 1–3).

The fragment O(1)C(8a)C(4a)N(1) in molecule (**1a**, d_1) is planar within 0.003(3) Å, atoms P(2) and C(3) deviate by −0.0273(7) and 0.613(3) Å to the opposite sides of this plane, therefore, the conformation of the six-membered heterocycle can be considered as a distorted *half-chair* (Figure 1). The deviation of the phosphorus atom from the plane of the tetraatomic fragment is small, and the penta-atomic fragment P(2)O(1)C(8a)C(4a)N(4) in molecule (**1a**, d_1) can be considered to be planar within 0.007(2) Å, from which atom C(3) of the oxazaphosphine ring deviates by −0.630(3) Å, and, therefore, the conformation of the heterocycle can be also characterized as the *sofa* (*envelop*). Atom O(2) is in the equatorial position (the deviation from the plane P(2)O(1)C(8a)C(4a)N(4) is −0.778(2)

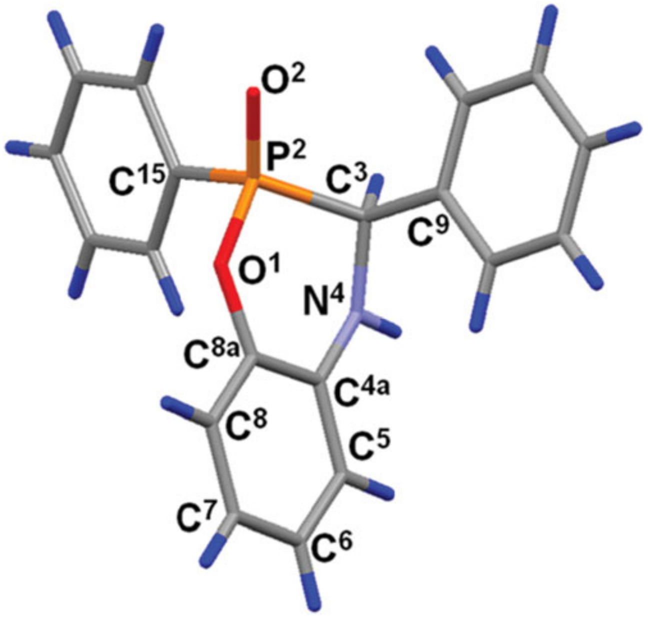


Figure 1 Crystal structure of (**1a**, d_1).

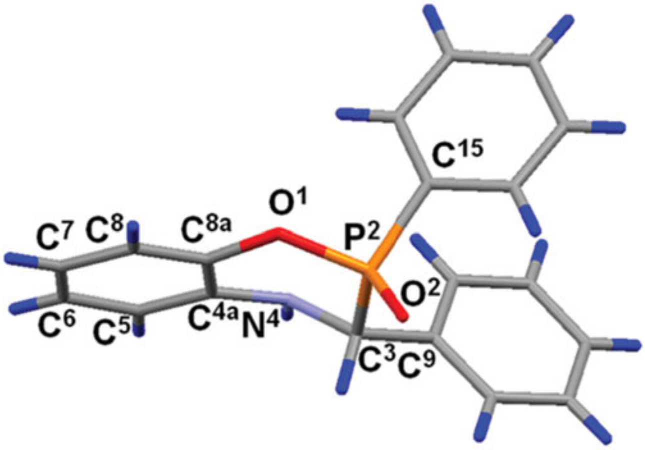


Figure 2 Crystal structure of (**1a**, d_2).

Å), the phenyl groups at atoms P(2) and C(3) are in the axial positions (the deviation of atoms C(9) and C(15) from the penta-atomic plane is 1.719(3) and −2.158(1) Å).

The crystal of compound (**1a**, d_2) contains two independent molecules (*A*, *B*) (only one molecule is shown in Figure 2). The conformation of both molecules, a distorted (non-symmetric) *boat*, contains a tetra-atomic planar fragment O(1)C(8a)C(4a)N(4). Two atoms of the heterocycle deviate from this fragment to the same side by different distances (P(2) and C(3) deviate by −0.615(1) and −0.941(5) Å in molecule *A* and by −0.601(1), −1.024(5)

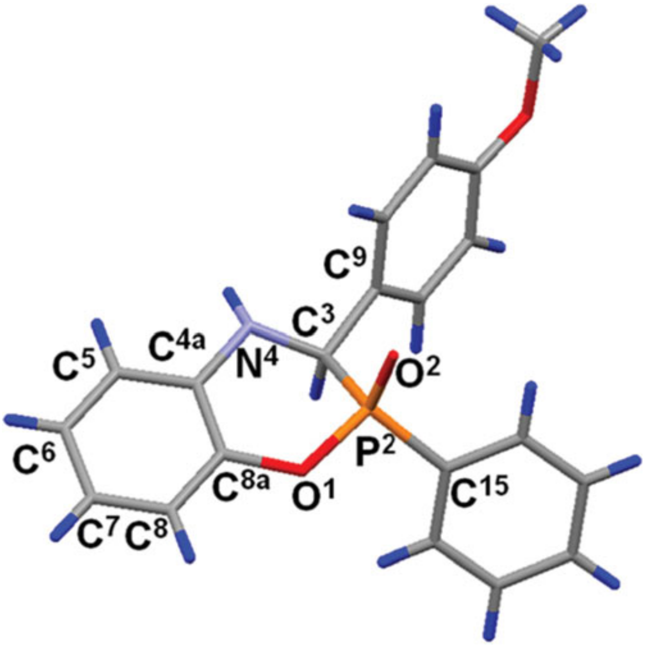


Figure 3 Crystal structure of (**1b**, d_1).

Å in molecule *B*), that secures the conformation of the distorted *boat*. Atom O(2) occupies the axial position in both molecules [it deviates from the plane O(1)C(8a)C(4a)N(4) by 1.813(3) Å (*A*) and 1.752(3) Å(*B*)]. The phenyl groups at atoms P(2) and C(3) are in the equatorial positions (atoms C(9) and C(15) deviate from the plane O(1)C(8a)C(4a)N(4) by 0.744(5), −0.852(5) Å (*A*), and −0.777(4), 1.143(5) Å (*B*).

In the crystal of compound (**1b**, d_1) (Figure 3), the conformation of the heterocycle differs from that observed in molecules (**1a**, d_1) and (**1a**, d_2): the fragment O(1)C(8a)C(4a)N(1) in molecule (**1b**, d_1) is planar within 0.004(2) Å, atoms P(2) and C(3) deviate to the opposite sides from this plane by −0.1586(5) and 0.677(2) Å, thus, the conformation of the six-membered heterocycle is a *half-chair*. At the same time, if to assume that molecule (**1b**, d_1), like in the structure (**1a**, d_1), has a pentaatomic fragment P(2)O(1)C(8a)C(4a)N(4) planar within 0.051(1) Å, then here the conformation of the heterocycle can be also described as a *sofa* (*envelop*) (remaining atom of the oxazaphosphine ring C(3) deviates by 0.773(2) Å). Atom O(2) is in the axial position (its deviation from the plane P(2)O(1)C(8a)C(4a)N(4) is −1.388(1) Å), the phenyl group at atom P(2) and the *para* methoxyphenyl substituent at atom C(3) occupy the equatorial positions (the deviation of atoms C(9) and C(15) from the five atomic plane is 1.057(2) and 0.777(2) Å, respectively).

Owing to the close values of R_f of diastereoisomers (**1c–e**), it appeared to be impossible to isolate the other one by column chromatography or by recrystallization. The structure of the compounds was confirmed by ^{1}H, ^{31}P NMR and chromatomass-spectrometry. There are the doublets corresponding to PCH-fragment in ^{1}H NMR spectra: 4.62 ppm, $^2J_{\mathrm{HP}}$ 18.4 Hz (**1c**, d_1), 4.64 ppm, $^2J_{\mathrm{HP}}$ 6.0 Hz (**1c**, d_2), 4.98 ppm, $^2J_{\mathrm{HP}}$ 10.3 Hz (1d, d_1), 5.01 ppm, $^2J_{\mathrm{HP}}$ 19.3 Hz (1d, d_2), 4.86 ppm, $^2J_{\mathrm{HP}}$ 9.9 Hz (**1e**, d_1), 5.03 ppm, $^2J_{\mathrm{HP}}$ 20.5 Hz (**1e**, d_2). Two singlets correspond to each compound in ^{31}P-{^{1}H} NMR spectra: δ_P 39.9 ppm (**1c**, d_1), 45.2 ppm (**1c**, d_2), 10.2 ppm (**1d**, d_1), 11.3 ppm (**1d**, d_2), 17.2 ppm (**1e**, d_1), 21.9 ppm (**1e**, d_2) ppm. There are the closely situated peaks in chromatograms of diastereoisomers with the same values of molecular masses [273 (**1c**), 289 (**1d**), 316 (**1e**)].

FUNDING

This study was supported by Russian Foundation for Basic Research (grant no. 13-03-90419).

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