ISSN 1070-3632, Russian Journal of General Chemistry, 2014, Vol. 84, No. 5, pp. 969–970. © Pleiades Publishing, Ltd., 2014.
Original Russian Text © Ya.A. Vereshchagina, V.F. Mironov, M.N. Dimukhametov, P.P. Onys'ko, Yu.V. Rassukanaya, D.V. Chachkov, 2014, published in Zhurnal Obshchei Khimii, 2014, Vol. 84, No. 5, pp. 877–878.

LETTERS
TO THE EDITOR

Quantum-Chemical Study of the Reaction of 2-Methylbenzo[*d*][1,3,2]dioxaphosphinin-4(4*H*)-one with Hexafluoroacetonimine

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Received January 16, 2014

Keywords: phosphinane, oxazaphosphepine, aminophosphonate, hexafluoroacetonimine, quantum-chemical calculations

DOI: 10.1134/S1070363214050338

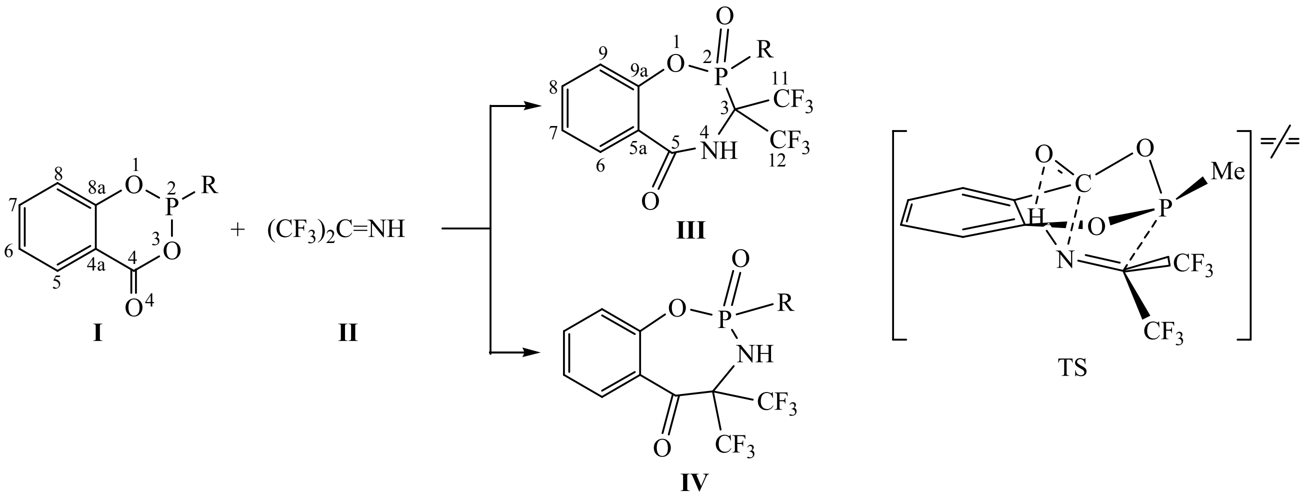
It is known that 2-R-benzo[*d*][1,3,2]dioxaphosphinan-4-ones **I** react with hexafluoroacetonimine (1,1,1,3,3,3-hexafluoropropan-2-imine) (**II**) to give derivatives of 2-R-3,4-dihydro-5(2*H*)-oxobenzo[*f*][1,4,2λ^5]oxazaphosphepine 2-oxide **III** or 2-R-3,4-dihydro-5(2*H*)-oxobenzo-[*f*][1,3,2λ^5]oxazaphosphepine 2-oxide **IV**, depending on the nature of R [1, 2] (Scheme 1). Taking into account that this method provides a simple and convenient synthetic approach to derivatives of α-aminophosphonic acids which exhibit diverse biological activity [3–5], we performed B3PW91/6-31G(d) DFT quantum-chemical calculations of the energies and transformation pathways of the starting compounds, products, and possible intermediates of the reaction of 2-methylbenzo[*d*][1,3,2]dioxaphosphinin-4(4*H*)-one (R = Me) with compound **II**.

According to the calculations, molecule **I** (R = Me) contains a virtually planar five-atomic fragment $O^3C^4C^{4a}C^{8a}O^1$ and the phosphorus atom deviating from this fragment: The dihedral angle between the $O^2C^4C^{4a}C^{8a}O^1$ and $O^1P^2O^3$ planes is about 30°. Thus, we can conclude that the heteroring in molecule **I** is in *a flattened chair* conformation which has the $C^4{=}O^4$ bond almost coplanar to the phenyl ring (the $C^5C^{4a}C^4O^4$ torsion angle is 9.0°). The exocyclic methyl substituent at the pyramidal P atom occupies an equatorial position, and the lone electron pair is axial.

The reaction product 3,3-bis(trifluoromethyl)-3,4-dihydro-2-methyl-5(2*H*)-oxobenzo[*f*][1,4,2λ^5]oxazaphosphepine 2-oxide (**III**), ΔE –96.7 kJ/mol, contains an almost planar six-atomic fragment $O^1C^{8a}C^{4a}C^4N^4C^3$, a planar phenyl ring, and the C=O coplanar to the latter (the $O^5C^5C^{5a}C^6$ torsion angle is 8.2°). The heteroring conformation is *flattened chair*. The $O^1P^2C^3$ forms with six-atomic heteroring plane a dihedral angle of 79°. The trifluoromethyl substituents deviate from this plane to opposite directions ($\angle C^{11}C^3N^4C^5$ –159.1°, $\angle C^{12}C^3N^4C^5$ 82.2°). The substituents at the P atom are *gauche* to the P=O bond. The P=O group is pseudoaxial, and the methyl substituent is pseudoequatorial.

According to the calculations, the reaction of compound **I** with hexafluoroacetonimine, unlike the reaction of its 2-phenyl analog with chloral [6, 7], occurs in one stage via asynchronous [3+2]-cycloaddition and is exothermal (heat effect 96.7 kJ/mol). The calculations predict initial formation of a prereaction complex (ΔE –18.1 kJ/mol) with a weak hydrogen bond between the $C^4{=}O^4$ oxygen and the

Scheme 1.



imine hydrogen (O^4–HN^1 2.060 Å). The planar imine molecule is oriented so that its nitrogen atom points to the C(O)–O heteroring fragment, i.e. the N^1=C^9 bond and C^4(O^4)–O^3 fragment get closer to each other. Further the prereaction complex via a transition state (TS) with Δ*E* 107.3 kJ/mol (zero was set on the total energy of the reagents at infinite distance from each other) forms the reaction product. In the transition state, the N^1=C^9 bond continues to approach the C^4 (O^4)–O^3 fragment (P^2–C^9 2.031 Å, O^4–HN^1 2.476 Å, N^1–C^4 2.113 A).

The B3PW91/6-31G(d) DFT calculations with full geometry optimization were performed using GAUSSIAN 09 suit [8]. Calculation of second derivatives was applied to verify that stationary points correspond to minima: In all cases the Hessian eigenvalues were positive. The calculations were performed at the Kazan Branch of the Interinstitutional Supercomputer Center of the Russian Academy of Sciences.

ACKNOWLEDGMENTS

The work was financially supported by the Russian Foundation of Basic Research (project no. 13-03-90419).

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