ISSN 1070-4280, Russian Journal of Organic Chemistry, 2014, Vol. 50, No. 4, pp. 608–610. © Pleiades Publishing, Ltd., 2014.
Original Russian Text © E.A. Ishmaeva, D.V. Chachkov, A.Z. Alimova, Ya.A. Vereshchagina, 2014, published in Zhurnal Organicheskoi Khimii, 2014, Vol. 50, No. 4, pp. 619–621.

SHORT COMMUNICATIONS

Mechanism of the Reaction of 3,3-Dimethyl-1-trimethylsilyl-2-trimethylsiloxy-1-phosphabut-1-ene with Chlorobis(*o*-phenylenedioxy)phosphorane

E. A. Ishmaeva[a], D. V. Chachkov[a, b], A. Z. Alimova[a], and Ya. A. Vereshchagina[a]

[a] *Kazan (Volga Region) Federal University, ul. Kremlevskaya 18, Kazan, 420008 Tatarstan, Russia*
e-mail: elenishmaeva@gmail.com

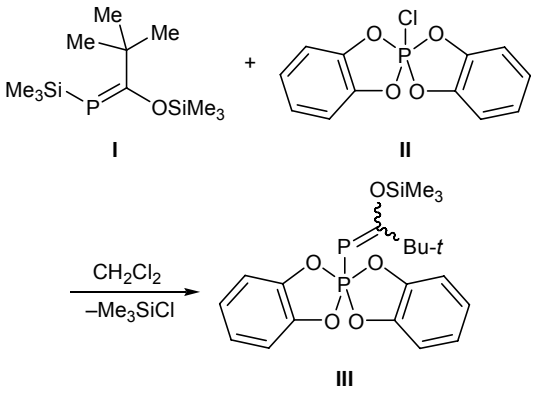
[b] *Kazan Branch, Joint Supercomputer Center of the Russian Academy of Sciences, ul. Lobachevskogo 2/31, Kazan, 420111 Tatarstan, Russia*

Received January 17, 2014

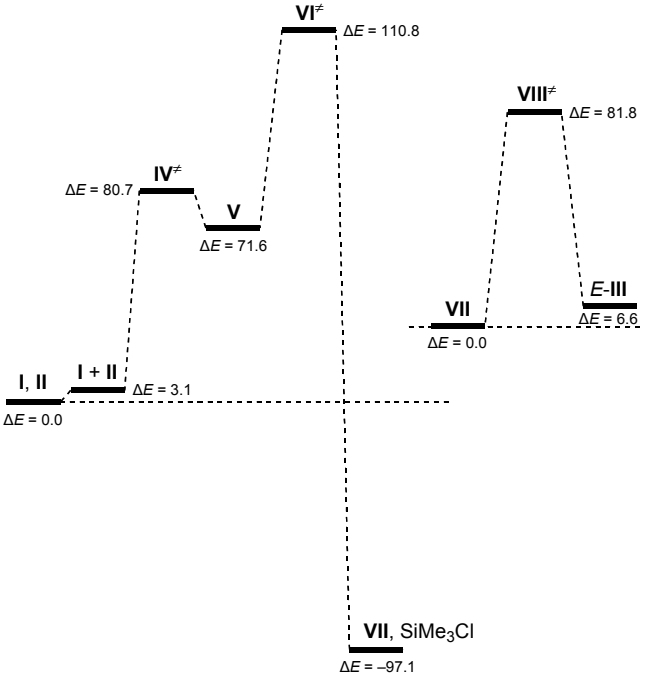
DOI: 10.1134/S1070428014040307

We have recently studied by quantum chemical methods the mechanism of the reaction of 3,3-dimethyl-2-trimethylsiloxy-1-trimethylsilyl-1-phosphabut-1-ene (**I**) with diethyl phosphite [1]. There are no published data on mechanisms of reactions of compound **I** with electrophilic reagents. We previously reported [2] that compound **I** reacts with an equimolar amount of chlorobis(*o*-phenylenedioxy)phosphorane under mild conditions to give the product of electrophilic replacement at the two-coordinate phosphorus atom, 3,3-dimethyl-1-bis(*o*-phenylenedioxy)-λ^5-phosphanyl-2-trimethylsiloxy-1-phosphabut-1-ene (**III**), and chlorotrimethylsilane (Scheme 1).

Scheme 1.

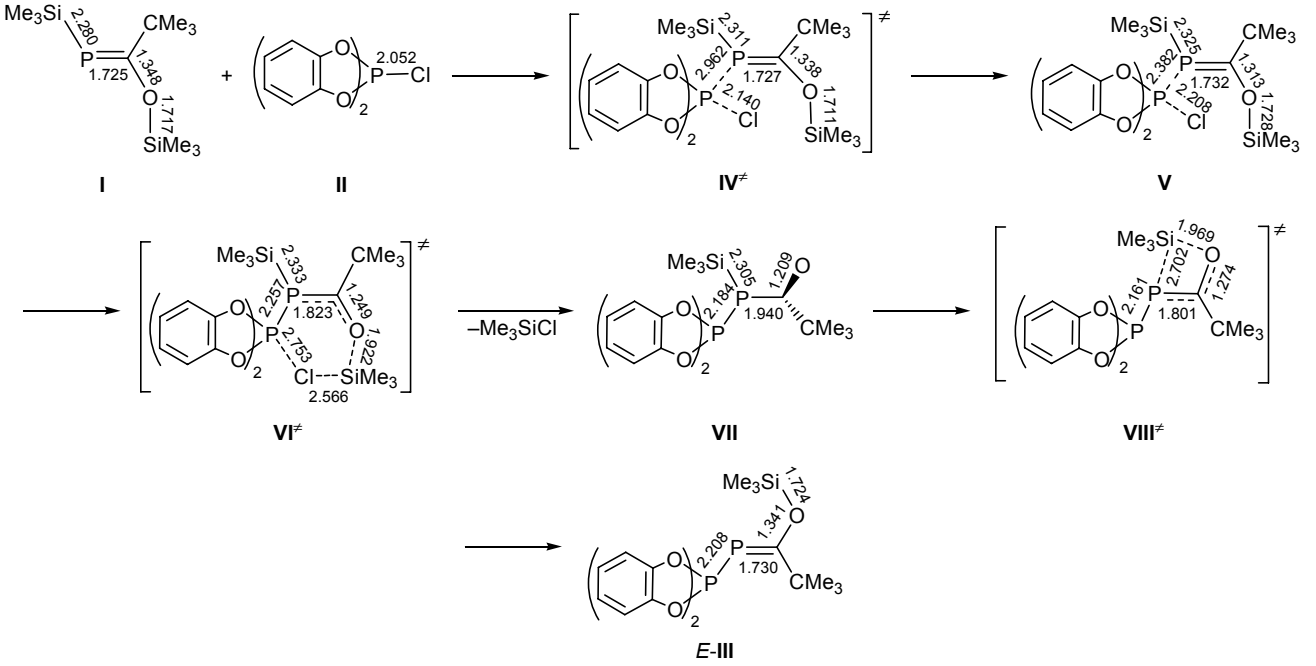


In the present work we performed a theoretical study of this reaction in terms of the density functional theory using the B3PW91 hybrid functional [3, 4] and standard 6-31G(*d*) basis set. All geometric parameters of the initial reactants, intermediate products, transition states, and final products were optimized. The structures localized on the potential energy surface were identified as minima or transition states by calculating the corresponding Hessian matrices (all positive eigenvalues for stable molecules and intermediates or at least one negative eigenvalue for transition states). The



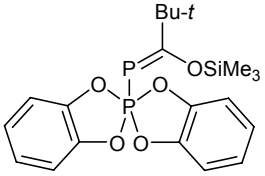
Energy profile (kJ/mol) of the reaction of 3,3-dimethyl-2-trimethylsiloxy-1-trimethylsilyl-1-phosphabut-1-ene (**I**) with chlorobis(*o*-phenylenedioxy)phosphorane (**II**).

Scheme 2.



calculations were carried out at the Kazan Branch of the Joint Supercomputer Center of the Russian Academy of Sciences (*http://wt.knc.ru*) using GAUSSIAN 09 software package [5].

The theoretical reaction mechanism is shown in Scheme 2 (bond lengths in the initial reactants, intermediate products, transition states, and final products are given in Å). The reaction includes three steps. In the first step, compound **I** reacts with **II** through transition state **IV**$^{\neq}$ with an energy of activation of 80.7 kJ×mol^{-1} to produce intermediate **V** with a P–P=C triad where the P–Cl bond is longer than in initial compound **II** (see figure). The second step is rearrangement of **V** into intermediate **VII** with a P–P–C triad (transition state **VI**$^{\neq}$; energy of activation 110.8 kJ×mol^{-1}). The P–C bond in **VII** is considerably longer (1.940 Å), and the P–P bond is shorter (2.184 Å), than in intermediate **V**. The rearrangement is accompanied by elimination of chlorotrimethylsilane. In the third state, intermediate **VII** undergoes rearrangement into the final product through transition state **VIII**$^{\neq}$ in which the P–P and P–C bonds are shorter than in **VII**; the energy of activation of this step is 81.8 kJ/mol. The P–C bond length in molecule **III** (1.730 Å) is typical of standard P=C bond (1.64–1.77 Å for two-coordinate phosphorus compounds, according to the X-ray diffraction data [6]). Correspondingly, the P–P bond extends to 2.208 Å. The energy of the *E* isomer of **III** is higher by 8.9 kJ/mol than the calculated energy of the most favorable conformer of the *Z* isomer of **III**.



Z-**III**

In summary, our DFT B3PW91/6-31G(*d*) quantum chemical study of the reaction of a stable two-coordinate phosphorus compound, 3,3-dimethyl-2-trimethylsiloxy-1-trimethylsilyl-1-phosphabut-1-ene, with chlorobis(*o*-phenylenedioxy)phosphorane showed that the process includes three steps and that the product is not the most energetically favorable isomer (its structure was not studied in [2]). In order to rationalize this result it is necessary to localize transition state for the transformation of the *E* isomer into *Z* isomer. Furthermore, it is reasonable to search for other possible conformations of transition states **IV**$^{\neq}$, **VI**$^{\neq}$, and **VIII**$^{\neq}$, which could lead to the more favorable *Z* isomer of **III**.

This study was performed under financial support by the Russian Foundation for Basic Research (project no. 13-03-00067-a).

REFERENCES

1. Ishmaeva, E.A., Chachkov, D.V., Alimova, A.Z., Vereshchagina, Ya.A., and Galkin, V.I., *Russ. J. Gen. Chem.*, 2012, vol. 82, p. 1951.

2. Popova, E.V., Mironov, V.F., Ishmaeva, E.A., and Patsanovskii, I.I., *Russ. J. Gen. Chem*., 1999, vol. 69, p. 48.

3. Becke, A.D., *Phys. Rev. A*, 1988, vol. 38, p. 3098.

4. Perdew, J.P., Burke, K., and Wang, Y., *Phys. Rev. B*, 1996, vol. 54, p. 16533.

5. Frisch, M.J., Trucks, G.W., Schlegel, H.B., Scuseria, G.E., Robb, M.A., Cheeseman, J.R., Scalmani, G., Barone, V., Mennucci, B., Petersson, G.A., Nakatsuji, H., Caricato, M., Li, X., Hratchian, H.P., Izmaylov, A.F., Bloino, J., Zheng, G., Sonnenberg, J.L., Hada, M., Ehara, M., Toyota, K., Fukuda, R., Hasegawa, J., Ishida, M., Nakajima, T., Honda, Y., Kitao, O., Nakai, H., Vreven, T., Montgomery, Jr., J.A., Peralta, J.E., Ogliaro, F., Bearpark, M., Heyd, J.J., Brothers, E., Kudin, K.N., Staroverov, V.N., Kobayashi, R., Normand, J., Raghavachari, K., Rendell, A., Burant, J.C., Iyengar, S.S., Tomasi, J., Cossi, M., Rega, N., Millam, J.M., Klene, M., Knox, J.E., Cross, J.B., Bakken, V., Adamo, C., Jaramillo, J., Gomperts, R., Stratmann, R.E., Yazyev, O., Austin, A.J., Cammi, R., Pomelli, C., Ochterski, J.W., Martin, R.L., Morokuma, K., Zakrzewski, V.G., Voth, G.A., Salvador, P., Dannenberg, J.J., Dapprich, S., Daniels, A.D., Farkas, Ö., Foresman, J.B., Ortiz, J.V., Cioslowski, J., and Fox, D.J. *Gaussian 09, Revision A.01*, Wallingford CT: Gaussian, 2009.

6. Markovskii, L.N., Romanenko, V.D., and Ruban, A.V., *Khimiya atsiklicheskikh soedinenii dvukhkoordinirovannogo fosfora* (Chemistry of Acyclic Two-Coordinate Phosphorus Compounds), Kiev: Naukova Dumka, 1988.