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# Mechanism of the Reaction of 3,3-Dimethyl-2-trimethylsiloxy-1-trimethylsilyl-1-phosphabut-1-ene with Diethyl Phosphite

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**Abstract**—The reaction of a stable two-coordinate phosphorus compound, 3,3-dimethyl-2-trimethylsiloxy-1-trimethylsilyl-1-phosphabut-1-ene, with diethyl phosphite was studied in terms of the density functional theory [DFT B3PW91/6-31G(*d*)]. A two-step mechanism of the reaction was established.

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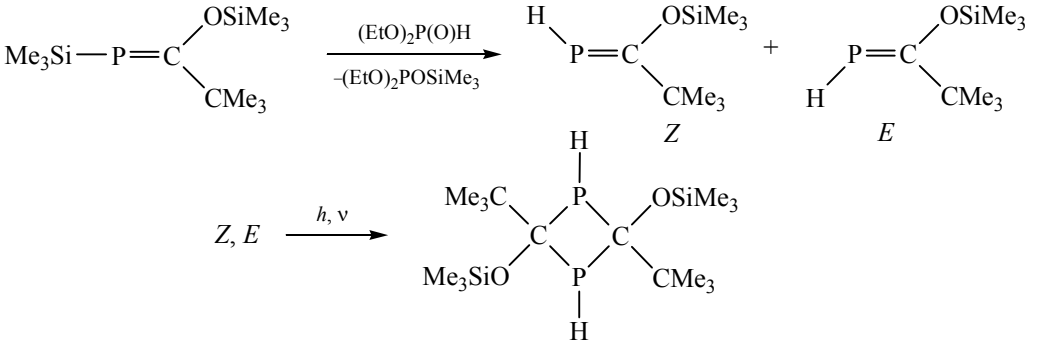
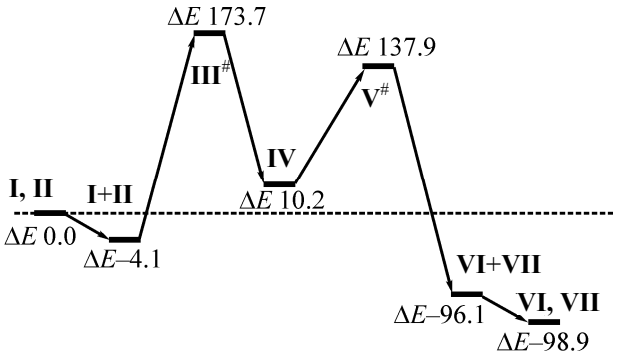
Phosphaalkenes may be regarded as informal analogs of olefins, and they possess properties intrinsic to both classical π-systems and three-coordinate tervalent phosphorus derivatives. Structural features of phosphaalkenes have been reviewed in detail in [1]. Despite numerous published data on the synthesis and structure of low-coordinate phosphorus compounds [1–3], problems related to their reactivity largely remain unexplored. It is known that 3,3-dimethyl-2-trimethylsiloxy-1-trimethylsilyl-1-phosphabut-1-ene, which is the key in the synthesis of one-coordinate phosphorus derivatives, reacts with proton-active compounds such as alcohols, acids, and amines via the cleavage of the P–Si and Si–O bonds [3, 4] leading to the exhaustive reduction product, *tert*-butyl-carbonylphosphine *t*-BuC(O)$PH_2$.

It was shown later [5, 6] that the reaction of phosphaalkene **I** with diethyl phosphite (**II**) at 20°C under argon involves selective reduction of the P–Si bond to afford 3,3-dimethyl-2-trimethylsiloxy-1-phosphabut-1-ene (**III**) as a mixture of *E* and *Z* isomers at a ratio of ~1 : 3 (Scheme 1). Reaction (1) is exothermic, and cyclodimerization (2) is initiated by irradiation.

**Scheme 1.**




We recently [7] performed a theoretical study on the reaction of substituted trimethylsilylphosphaethene **I** with diethyl phosphite and phosphorus(III) chlorides and determined thermodynamic parameters of these reactions; however, mechanistic details, including all elementary steps and the corresponding transition state structures, were not studied. In the present article we report on the results of DFT study on the reaction of **I**

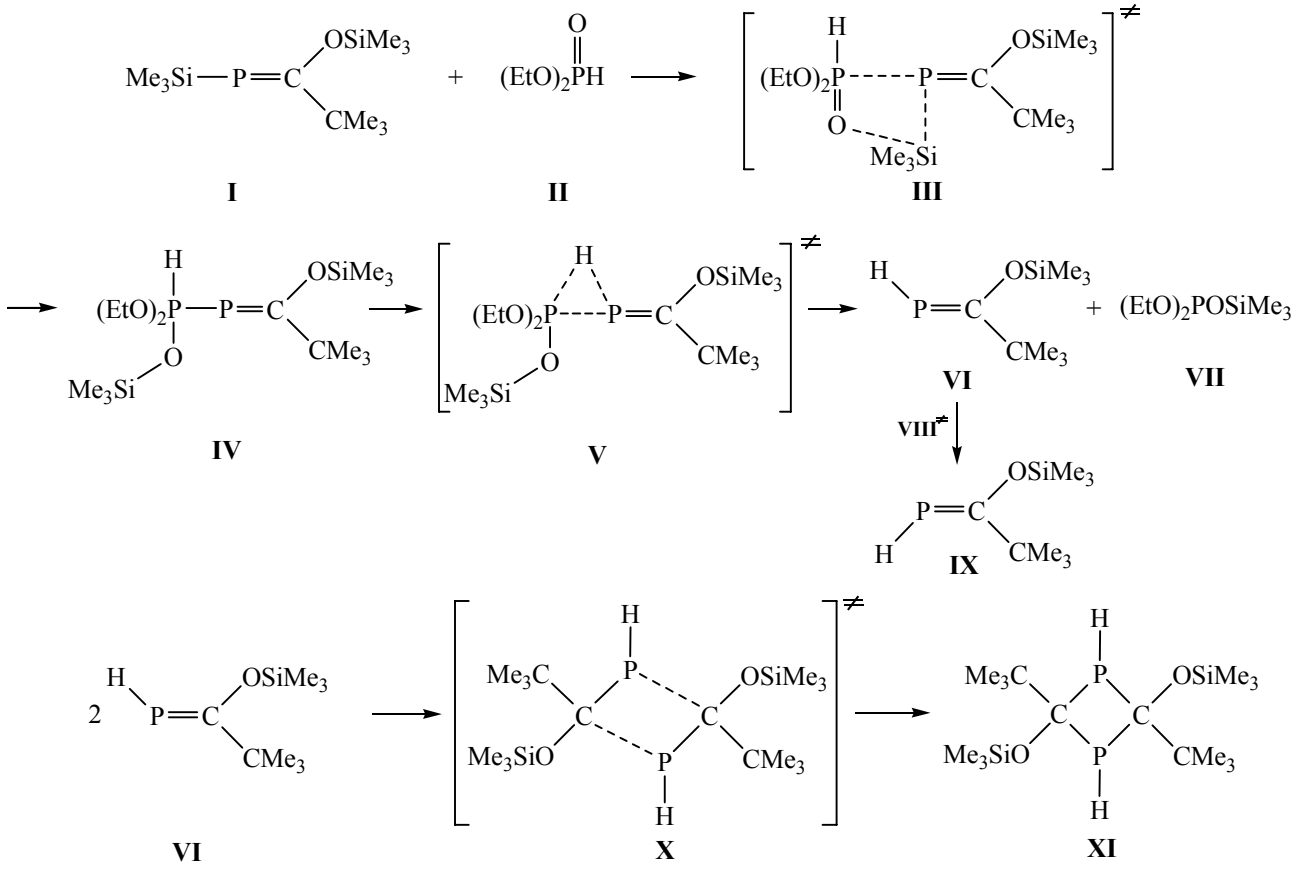



Energy diagram for the formation of phosphaalkene **VI** from 2-*tert*-butyl-2-trimethylsiloxy-1-trimethylsilylphosphaethene (**I**) and diethyl phosphite (**II**).

with phosphite **II** using the B3PW91 hybrid functional [8, 9] and standard 6-31G(*d*) basis set. Geometric parameters of all molecular structures were completely optimized. Stationary points on the potential energy surface were identified by calculating Hessian matrices (all positive Hessian eigenvalues for stable molecules and intermediates and at least one imaginary eigenvalue for transition states). The calculations were performed using GAUSSIAN 09 software package [10] at the Kazan Branch, Joint Supercomputer Center of the Russian Academy of Sciences (*http://wt.knc.ru*).

It was found that, unlike the scheme proposed in [6, 7], reaction (1) occurs in two steps (Scheme 2). In the first step, relatively stable intermediate **IV** is generated from compounds **I** and **II** through pre-reaction complex [**I** + **II**] and transition state **III**$^{\neq}$ involving transfer of the $Si(CH_3)_3$ group to the phosphite oxygen atom. The second step is characterized by somewhat lower energy of activation, and it includes hydrogen transfer from the five-coordinate phosphorus atom in **IV** to the two-coordinate phosphorus through transition state **V**$^{\neq}$. Decomposition of post-reaction complex [**VI** + **VII**] yields $\lambda^3$-phosphanylidene derivative (*Z*)-**VI** and diethyl trimethylsilyl phosphite (**VII**). The energy diagram of the examined processes is shown in figure. The energy of infinitely distant molecules **I** and **II** was set at zero, so that we were able to estimate both the stability of intermediate **IV** and the heat effect of the overall process.

**Scheme 2.**



According to the calculations, *Z* isomer **VI** can be converted into slightly less stable (by 2.1 kJ/mol) *E* isomer **IX** through a barrier of 139.0 kJ/mol.

Reaction (2) with formation of dimer **XI** occurs in one step through transition state $\mathbf{X}^{\neq}$ and is characterized by a fairly high energy of activation (234.6 kJ/mol) and a weak endothermic effect (0.2 kJ/mol), which is generally consistent with the experimental data, i.e., low concentration of dimer **XI** in the reaction mixture on exposure to light (low intensity of the corresponding $^{31}$P NMR signal [5]).

The proposed scheme does not rationalize the role of *E* isomer **IX**. The latter could be formed only assuming a different configuration of the reaction center and hence different configuration of the transition state. It will be the subject of our further studies.

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