

# Theoretical and Experimental Investigation of Reactions between Dialkyl Phosphites and *tert*-Butylphosphaethyne

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Received May 6, 2003

**Abstract**—Experimental and theoretical study of reactions between dialkyl phosphites and *tert*-butylphosphaethyne revealed that the preferred reaction route resulted in formation of a phosphalkene containing a fragment C=P–P(O) including simultaneously a bicoordinate and tetracoordinate phosphorus.

Chemical characteristics of the monocoordinate phosphorus are studied mainly in processes of complex formation and cycloaddition [1–7]. Publications on addition of proton-donor reagents X–H across the triple C≡P bond in phosphalkynes R–C≡P are still scarce [5, 8–10]. Preliminary data on a reaction of *tert*-butylphosphaethyne with diethyl phosphite that we obtained by means of <sup>31</sup>P NMR procedure and by semiempirical (PM3) calculation provided ambiguous results [9]. Therefore we carried out a repeated more detailed investigation of the diethyl phosphite reaction with *t*-Bu–C≡P using <sup>31</sup>P NMR and *ab initio* quantum-chemical calculations in comparison with acetylenes and other formal analogs of phosphalkynes.

Published data show that acetylenes (1-hexyne, 1-heptyne, and phenylacetylene) add dialkyl phosphites in the presence of benzoyl peroxide or under UV irradiation in anti-Markownikoff mode affording 1:1 adducts at the equimolar reagents ratio [11]. At 10-fold excess under stringent conditions (140–180°C, UV irradiation or peroxide) 1,2-diphosponalkanes were obtained [12].

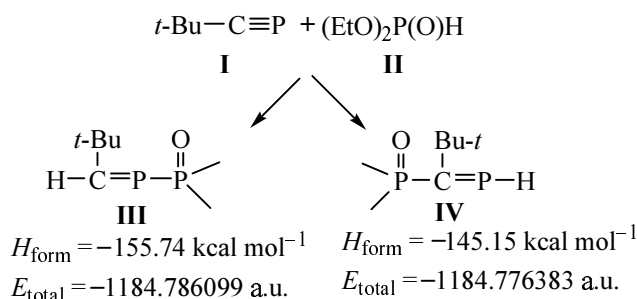
<sup>31</sup>P NMR study of the reaction between phosphalkyne **I** and diethyl phosphite (**II**) revealed that under mild conditions with no catalyst the reaction did not occur, same as with acetylenes and the other formal analogs of phosphalkynes. However the addition of metallic sodium (base catalyst) to the reaction mixture containing 5-fold excess of diethyl phosphite resulted in reaction proceeding for 7 days. As we show further, the process occurs with intermediate formation of phos-

phorylated phosphalkene **III**. It should be noted that the latter fact may testify to a certain similarity in the mechanisms of both reactions. The probable formation routes presented on Schemes 1 and 2 include both experimentally obtained compound **III** and hypothetical reaction products **IV–VII** considered in quantum-chemical calculations of reactions between one or two dimethyl phosphite molecules and phosphalkyne **I**. The  $\Delta H_{\text{form}}$  values were calculated by PM3 procedure.

The calculations including optimization of geometric parameters of all assumed final structures **III–VII** were performed by nonempirical method taking into account the electron correlation within the framework of density functional theory B3LYP [13, 14] using a polarized basis set 6-31(d).

The performed quantum-chemical calculations for the reaction of dimethyl phosphite with phosphalkyne **I** taking into account the *E,Z*-isomerism in conformers with

Scheme 1.



Geometric parameters of molecular structures **III**–**VII** optimized in the framework of B3LYP/6-31G(d) method, bond lengths in Å, bond and dihedral angles in degrees

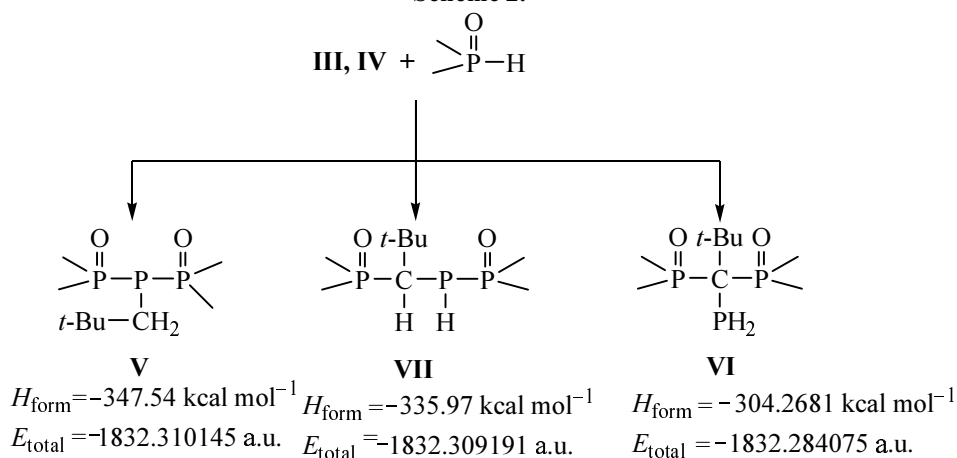
<b>III</b>		<b>IV</b>		<b>V</b>		<b>VI</b>		<b>VII</b>	
C=P	1.69	P–C	1.82	P–P	2.21	P=O	1.48	P–C	1.84
P–P	2.22	C=P	1.69	P=O	1.48	P–C	1.87	P=O	1.49
P=O	1.49	P–H	1.42	P–CH <sub>2</sub>	1.89	C– <i>t</i> -Bu	1.62	P–P	2.22
C– <i>t</i> -Bu	1.51	C– <i>t</i> -Bu	1.54	O=P–P	115.28	C–PH <sub>2</sub>	1.94	P–H	1.42
C=P–P	99.3	P=O	1.49	P–P–P	102.48	O=P–C	117.61	C– <i>t</i> -Bu	1.58
P–P=O	113.7	O=P–C	119.16	P–C– <i>t</i> -Bu	114.80	P–C–PH <sub>2</sub>	106.08	O=P–C	119.30
P=C– <i>t</i> -Bu	126.0	–C=P	120.50	O=P–P–P	170.43	<i>t</i> -Bu–C–PH <sub>2</sub>	110.15	P–P=O	116.92
P=C–H	120.29	P=C– <i>t</i> -Bu	121.84	P–P–P=O	–87.05	<i>t</i> -Bu–C–P	112.18	P–C–P	106.34
C=P–P=O	–135.6	C=P–H	98.23	P–P–C– <i>t</i> -Bu	102.78	O=P–C–P	–46.88	C–P–P	102.17
<i>t</i> -Bu–C=P–P	178.36	O=P–C=P	179.91	<i>t</i> -Bu–C–P–P	–151.15	P–C–P=O	162.25	P–C–H	105.21
		O=P–C– <i>t</i> -Bu	–0.09	O=P–P–CH <sub>2</sub>	–82.37	O=P–C–PH <sub>2</sub>	161.07	P–C– <i>t</i> -Bu	114.84
				CH <sub>2</sub> –P–P=O	167.72	<i>t</i> -Bu–C–P=O	–72.17	P–P–H	93.14
								O=P–C–P	85.79
								C–P–P=O	–111.83
								<i>t</i> -Bu–C–P–H	–53.88
								O=P–P–H	151.17
								O=P–C– <i>t</i> -Bu	–40.72
								H–C–P–H	66.24

various orientation of P=C and P=O bonds (*s-cis*- and *s-trans*-) demonstrated that among the primary addition products (**III** and **IV**) the compound containing a P–P bond (**III**) as compared with isomer **IV** with a P–C bond is more energetically stable (by 6.1 kcal mol<sup>–1</sup>).

Nonempirical calculation of products of the following probable reaction stage (addition of the second dimethyl phosphite molecule) show that tertiary phosphine **V** is more feasible than primary phosphine **VI** by 16.4 kcal mol<sup>–1</sup>. Note that we obtained similar results in the study of the reaction with the use of semiempirical quantum-chemical methods MNDO, AM1, and PM3 also carried

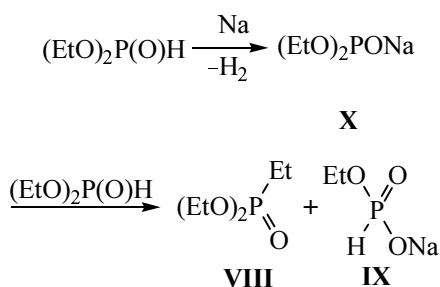
out with optimization of the geometric parameters [9] (see table). The experiment confirmed in general the conclusions theoretically drawn. In the <sup>31</sup>P-<sup>1</sup>H} NMR spectrum of the reaction mixture after disappearance of the signal belonging to the initial phosphalkyne (δ<sub>p</sub> –69 ppm) appeared two doublets at δ<sub>p</sub> 41.3 (<sup>1</sup>J<sub>PP</sub> 205.3) and δ<sub>p</sub> –36.5 ppm (<sup>1</sup>J<sub>PP</sub> 205.3 Hz) with an equal integral intensity ratio (1:1). The signals may be assigned to compound **III**, the product of addition of a single diethyl phosphite molecule. The spectra recorded without decoupling from protons contain the same doublets with slight broadening indicating that no direct P–H bonds

Scheme 2.



exist in this compound. Apparently the downfield signal corresponds to the tetracoordinate phosphorus, and that in the high field belongs to the bicoordinate one. No products of **V** and **VII** type resulting from addition to the phosphalkyne of two diethyl phosphite molecules formed in the reaction, in conformity to the data we had previously obtained in reaction of diethyl phosphite with a compound of bicoordinate phosphorus possessing a similar structure, 2-*tert*-butyl-1-trimethylsilyl-2-trimethylsiloxy-1-phosphaethene [15].

It should be noted that the reaction of compound **I** with diethyl phosphite is in general a more complicated process and involves side reactions. One among these side reactions is a partial conversion of diethyl phosphite into diethyl ethylphosphonate. For instance, according to the data in [16–18] diethyl phosphite at prolonged contact with metallic sodium undergoes partial isometization into O,O-diethyl ethylphosphonate (**VIII**) and sodium salt of ethyl phosphite (**IX**). The isomerization occurs along anionic chain mechanism.



This process is revealed by the fast disappearance in the  $^{31}\text{P}$  NMR spectrum of the signals from phosphite anion (**X**) ( $\delta_{\text{p}}$  148.7 ppm) and by appearance of a signal at  $\delta_{\text{p}}$  33.8 ppm corresponding to phosphonate **VIII**, and also of a signal at  $\delta_{\text{p}}$  6.2 ppm ( $^1J_{\text{PH}}$  653.2 Hz) belonging to salt **IX**. At prolonged accumulation of the spectrum we also distinguished signals at  $\delta_{\text{p}}$  28.2, 30.9, 139.1, and 128.7 ppm. The appearance of these signals is due to complex processes of initial phosphite alkylation with salt **X**. Note that these processes are partially described in the literature but they have not been unambiguously interpreted save the above mentioned isomerization of diethyl phosphite into diethyl ethylphosphonate. Besides due to the low concentration of initial phosphalkyne **I** becomes important the presence of ethanol impurity that can be present in the initial diethyl phosphite or may arise during its isomerization by a not yet clear mechanism. In this case the presence of sodium salt **X** apparently facilitates further reaction with ethanol either

of compound **III** or of initial phosphalkyne **I**. In all likelihood just one of these reactions causes the appearance in the  $^{31}\text{P}$ - $\{^1\text{H}\}$  NMR spectrum of the reaction mixture of one more signal at  $\delta_{\text{p}}$  -162.3 ppm that is split into a triplet with a coupling constant  $^1J_{\text{PH}}$  197.6 Hz in the  $^{31}\text{P}$  NMR spectrum recorded without decoupling from protons. This signal we assigned to a primary phosphine  $\text{PH}_2\text{-CH}(\text{OEt})\text{-Bu-}t$  (**XI**).

Carboxylic acids nitriles in the classic conditions of Pudovik reaction (in the presence of bases) do not take up dialkyl phosphites. However in reactions of sodium dialkyl phosphites with methyl-, phenyl-, and benzyl cyanides products arise originating from the addition at the multiple bond that on acidifying are capable to undergo aminophosphonate-amidophosphate rearrangement [19].

Diethyl phosphite addition to acetonitrile in the presence of hydrogen chloride was also described [20], that resulted in bis(dialkylphosphonyl)alkylamines. Here the diethyl phosphite added to the adduct of the nitrile with hydrogen chloride (at the HCl to  $\text{CH}_3\text{C}\equiv\text{N}$  ratio equal to 1:1). The structure of the adduct may vary from ketenimine and carbocation to nitrilium ion and immonium halide.

Although the mechanisms of diethyl phosphite reactions with acetylenes and phosphalkynes are different, the regiochemistry of the first addition stage is similar: products of 2-addition are obtained (with a C–H bond). Unlike that reactions with nitriles afford compounds of 1-addition (with an N–H bond).

Thus the new experimental data obtained and also *ab initio* quantum-chemical calculation unambiguously indicate, that the regiochemistry of the first stage in dialkyl phosphite reaction with acetylenes, nitriles, and phosphalkynes is similar.

## EXPERIMENTAL

$^{31}\text{P}$  and  $^{31}\text{P}$ - $\{^1\text{H}\}$  NMR spectra were registered on spectrometer Varian Unity-300 at operating frequency 121.42 MHz, external reference 85%  $\text{H}_3\text{PO}_4$ . *tert*-Butylphosphaethyne was prepared by procedure from [21], and its characteristics were consistent with the published data.

**Reaction of *tert*-butylphosphaethyne (**I**) with diethyl phosphite (**II**).** Into a standard NMR tube of 5 mm size under constant argon flow through a thin capillary was charged 0.32 g (0.064 mmol) of 20% *tert*-butylphosphaethyne solution in dimethoxyethane and 0.44 g (3.2 mmol) of diethyl phosphite. To the mixture

obtained 0.024 g (1.06 mmol) of metallic sodium was added, and the reaction mixture was heated for 3 h at 50–60°C. Then the reaction mixture was subjected to  $^{31}\text{P}$  NMR analysis. In the spectrum of the reaction mixture after disappearance of the signal from the initial phosphacetylene ( $\delta_{\text{p}} -69$  ppm) were observed two doublets at  $\delta_{\text{p}} 41.3$  ( $^1J_{\text{pp}} 205.3$ ) and  $\delta_{\text{p}} -36.5$  ppm ( $^1J_{\text{pp}} 205.3$  Hz) in 1:1 ratio belonging to compound **III**.

The study was carried out under financial support of the Ministry of Education of Russia (grants nos. NSh-750.2003.3 and UR.05.01.016).

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