

SHORT
COMMUNICATIONSReaction of Diethyl 3-Methylbuta-1,2-dien-1-ylphosphonate
with Ethane-1,2-diamineN. G. Khusainova^a, I. A. Litvinov^b, D. B. Krivolapov^b, E. A. Berdnikov^a, Yu. A. Sokolov^a,
S. M. Rybakov^a, and R. A. Cherkasov^a^a Butlerov Institute of Chemistry, Kazan State University, ul. Kremlevskaya 18, Kazan, 420008 Tatarstan, Russia
e-mail: narkis.khusainova@ksu.ru^b Arbuzov Institute of Organic and Physical Chemistry, Kazan Research Center, Russian Academy of Sciences,
ul. Arbuzova 8, Kazan, 420088 Tatarstan, Russia

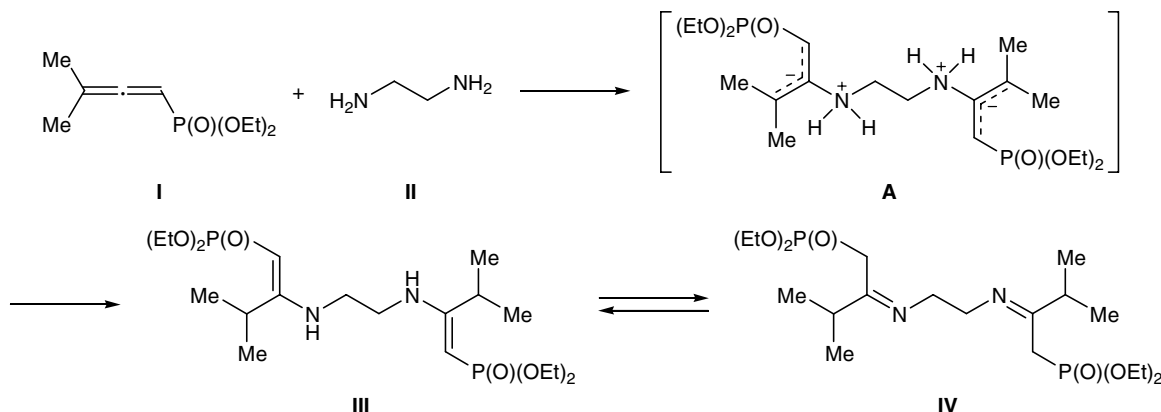
Received October 3, 2006

DOI: 10.1134/S1070428007030256

With the goal of obtaining new potential biologically active alkenylphosphonates having nitrogen-containing groups in the β -position with respect to the phosphoryl fragment [1], we examined the reaction of diethyl 3-methylbuta-1,2-dien-1-ylphosphonate (**I**) with ethane-1,2-diamine (**II**). It is known that reactions of primary and secondary amines with unsaturated four-coordinate phosphorus acid derivatives [2] provide the most accessible synthetic route to β -aminoalkenylphosphonates [3]. By heating diethyl 3-methylbuta-1,2-dien-1-ylphosphonate (**I**) with diamine **II** at 85–90°C until the allene absorption band (1955 cm^{-1}) disappeared from the IR spectrum of the reaction mixture we obtained a crystalline substance with mp 133°C. Found, %: C 50.95; H 9.23. $\text{C}_{20}\text{H}_{42}\text{N}_2\text{O}_6\text{P}_2$. Calculated, %: C 51.28; H 8.97. X-Ray analysis of the product showed that its molecule consists of two 1-diethoxyphosphoryl-3-methylbut-1-ene fragments linked through an ethylenediamine bridge (see figure). The

molecule in crystal occupies a partial position in the symmetry center. The adduct has the structure of tetraethyl *N,N'*-ethylenebis[(*E*)-2-amino-3-methylbut-1-en-1-ylphosphonate] (**III**) with *trans* arrangement of the phosphoryl and amine fragments. The phosphorus atom has a distorted tetrahedral configuration typical of phosphonates. Selected bond lengths and bond and dihedral angles in molecule **III** are given in table. Molecules **III** in crystal are linked through intermolecular hydrogen bonds $\text{N-H}\cdots\text{O}$ which give rise to infinite dimeric zigzag chains. The hydrogen bond has the following parameters: $\text{N}^6\text{--H}^6\cdots\text{O}^{1'}$ ($x, 1 - y, 1/2 + z$), $\text{N}^6\text{--H}^6$ 0.84(2), $\text{H}^6\cdots\text{O}^{1'}$ 2.04(2), $\text{N}^6\cdots\text{O}^{1'}$ 2.858(2) Å, $\angle\text{N}^6\text{H}^6\text{O}^{1'}$ 163(2)°.

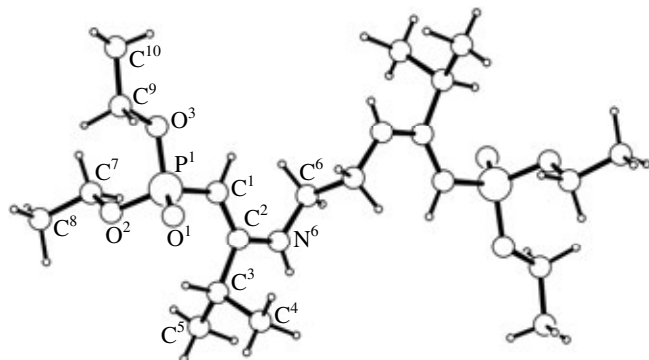
Presumably, zwitterion **A** formed as a result of attack by diamine **II** on the central carbon atom in the allene system of phosphorylbutadiene **I** is stabilized as enamine **III**. According to the ^1H and ^{31}P NMR data, enamine **III** in chloroform solution exist in tautomeric



Selected bond lengths and bond and dihedral angles in the molecule of tetraethyl *N,N'*-ethylenebis[(*E*)-2-amino-3-methylbut-1-en-1-ylphosphonate] (**III**) in crystal

Bond	<i>d</i> , Å	Bond	<i>d</i> , Å
P ¹ –O ¹	1.470(1)	N ⁶ –C ⁶	1.451(2)
P ¹ –O ²	1.584(1)	C ¹ –C ²	1.362(2)
P ¹ –O ³	1.578(1)	N ⁶ –H ⁶	0.84(2)
P ¹ –C ¹	1.745(2)	N ⁶ –C ²	1.358(2)
Angle	ω, deg	Angle	ω, deg
O ¹ P ¹ O ²	106.05(7)	O ² P ¹ O ³	105.31(7)
O ¹ P ¹ O ³	113.74(8)	O ² P ¹ C ¹	111.01(7)
O ¹ P ¹ C ¹	118.99(7)	O ³ P ¹ C ¹	101.05(7)
P ¹ C ¹ C ²	123.7(1)	N ⁶ C ² C ¹	123.4(1)
C ² N ⁶ C ⁶	125.7(1)	N ⁶ C ² C ³	114.5(1)
Angle	φ, deg	Angle	φ, deg
O ¹ P ¹ C ¹ C ²	–56.41(18)	P ¹ C ¹ C ² N ⁶	179.52(13)
C ⁶ N ⁶ C ² C ¹	–4.16(27)	P ¹ C ¹ C ² C ³	–1.58(24)

equilibrium with imino form **IV**. In the ¹H NMR spectrum of the product in CDCl₃, the olefinic proton in the α-position with respect to the phosphoryl group gives a doublet at δ 3.62 ppm (²*J*_{PH} = 10.4 Hz). The doublet signal at δ 3.01 ppm (²*J*_{PH} = 22.8 Hz) corresponds to protons of the methylene group at the phosphorus atom in tautomer **IV**. The spectrum contained no doublet signals in the region δ 1.8–2.0 ppm, which are typical of two nonequivalent methyl groups at *sp*²-hybridized carbon atom; therefore, the structure having C²=C³ double bond can be ruled out. In the ³¹P NMR spectrum of the adduct we observed two signals at δ_p 26.5 and 23.8 ppm, which were assigned to the enamine (**III**) and imine tautomers (**IV**), respectively. An analogous tautomeric equilibrium was reported by us previously for the addition products obtained from



Structure of the molecule of tetraethyl *N,N'*-ethylenebis-[(*E*)-2-amino-3-methylbut-1-en-1-ylphosphonate] (**III**) according to the X-ray diffraction data.

3-methylbuta-1,2-dien-1-ylphosphonates and 2-aminoethanol or butylamine [3].

The IR spectra were recorded on a UR-20 spectrometer. The ¹H and ³¹P NMR spectra were obtained from solutions in CDCl₃ on a Varian Unity-300 spectrometer at 300 and 121.42 MHz, respectively; the chemical shifts were measured relative to the residual solvent signal (¹H) and 85% H₃PO₄ (³¹P, external reference).

X-Ray diffraction data for compound III. Monoclinic crystals, C₂₀H₄₂N₂O₆P₂, with the following unit cell parameters (20°C): *a* = 13.279(2), *b* = 18.126(3), *c* = 11.096(2) Å; β = 96.51(2)°; *V* = 2653.5(8) Å³; *d*_{calc} = 1.17 g/cm³; *Z* = 4; space group *C2/c* (the molecule occupies a partial position in the symmetry center). The unit cell parameters and intensities of 2935 independent reflections (2161 reflections with *I* ≥ 3σ) were measured on an Enraf–Nonius CAD-4 diffractometer (ω-scanning, θ ≤ 74.26°, λCuKα, graphite monochromator). A correction for absorption was introduced empirically (μ_{Cu} = 17.7 cm^{–1}). The structure was solved by the direct method using SIR program [4] and was refined by the full-matrix least-squares procedure using MolEN software package [5]. The positions of non-hydrogen atoms were refined in anisotropic approximation. Hydrogen atoms were visualized from the difference electron density series, and their positions were refined in isotropic approximation at the final refinement iterations. The final divergence factors were *R* = 0.038 and *R*_w = 0.050 (from 2161 reflections with *F*² ≥ 3σ²). All calculations were performed on an Alpha Station 200 computer. The molecular structure was plotted using PLATON program [6].

REFERENCES

1. *Aminophosphonic and Aminophosphinic Acids: Chemistry and Biological Activity*, Kukhar, V.P. and Hudson, H.R., Eds., New York: Wiley, 2000.
2. Pudovik, A.N. and Denisova, G.M., *Zh. Obshch. Khim.*, 1953, vol. 23, p. 263.
3. Khusainova, N.G., Mostovaya, O.A., Berdnikov, E.A., Litvinov, I.A., Krivolapov, D.B., and Cherkasov, R.A., *Russ. J. Org. Chem.*, 2005, vol. 41, p. 1260.
4. Altomare, A., Cascarano, G., Giacovazzo, C., and Viterbo, D., *Acta Crystallogr., Sect. A*, 1991, vol. 47, p. 744.
5. Straver, L.H. and Schierbeek, A.J., *MolEN. Structure Determination System*, Nonius B.V., 1994, vol. 1, p. 2.
6. Spek, A.L., *Acta Crystallogr., Sect. A*, 1990, vol. 46, p. 34.