ISSN 1070-3632, Russian Journal of General Chemistry, 2013, Vol. 83, No. 7, pp. 1324–1329. © Pleiades Publishing, Ltd., 2013.
Original Russian Text © V.A. Zagumennov, N.A. Sizova, O.A. Lodochnikova, D.B. Krivolapov, I.A. Litvinov, 2013, published in Zhurnal Obshchei Khimii, 2013, Vol. 83, No. 7, pp. 1071–1076.

Diphosphonioiminobornane Diperchlorate: Electrosynthesis, Crystal Structure, and Hydrolysis

V. A. Zagumennov[a], N. A. Sizova[a], O. A. Lodochnikova[b], D. B. Krivolapov[b], and I. A. Litvinov[b]

[a] *Kazan (Volga) Federal University, ul. Kremlevskaya 18, Kazan, Tatarstan, 420008 Russia*
e-mail: zagum@ksu.ru

[b] *Arbuzov Institute of Organic and Physical Chemistry, Russian Academy of Sciences, Kazan, Tatarstan, Russia*

Received June 21, 2012

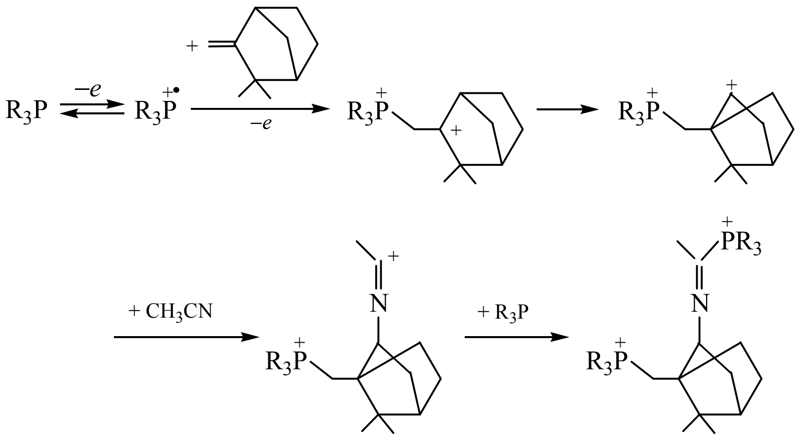
Abstract—On of the products of electrochemical phosphorylation of camphene was 2-(*C*-methyl-*C*-trialkylphosphonio)methyleneimino-10-trialkylphosphoniomethyl)bornane diperhlorates. A mechanism of their formation was suggested consisting in the rearrangement of the intermediate camphenylphosphonium dication followed by selective addition of acetonitrile and a second trialkylphosphine molecules. The diperhlorate hydrolysis was found to lead to the synthesis of 2-acetamido-10-trialkylphosphoniobornane perchlorates. The 2-(*C*-methyl-*C*-tripropylphosphonio)methyleneimino-10-tripropylphosphoniomethyl)bornane and 2-acetamido-yl-10-tripropylphosphoniobornane structures were established by the X-ray diffraction study.

DOI: 10.1134/S1070363213070049

We have found previously that the anode-generated trialkylphosphine cation radicals interact with camphene to afford two classes of products, the camphenylphosphonum salts, formed through elimination of a proton [1], and phosphinimino-terpenylphosphonium salts formed probably [2], at the rearrangement or disclosure the terpene backbone. The exact structure of the phosphiniminoterpenylphosphonium compounds (**I**) could not be determined. However, in an experiment using tripropylphosphine optimum conditions for chromatographic separation were selected and we succeeded in the isolation of an almost pure sample of compound **I** (δ_P 33.9 and 31.7 ppm) as a fine powder. To establish the exact structure of compound **I** by the method of X-ray diffraction (XRD) we attempted to obtain crystals of this compound. Crystalline samples of **I** were obtained by crystallization from methanol as colorless crystals. The structure of compound **I** presented in Figure 1 was solved in the space group $P2_1/n$. Geometric parameters (bond lengths and bond angles) of the molecule **I** are listed in table.

As seen, compound **I** is 2-(*C*-methyl-*C*-tripropylphosphonio)methyleneimino-10-tripropylphosphoniomethyl)bornane. The compound bears a phosphonium group at the exocyclic carbon atom and an iminophosphonium group at the carbon C^2. The presumed mechanism of formation of **I** is represented by scheme (1). The cation radicals formed initially by the anodic oxidation of tertiary phosphine add to the exocyclic double bond of the camphene molecule. Further additional oxidation of the adduct leads to a dications intermediate, which undergoes camphene-bornane rearrangement along the Wagner–Meerwein mechanism, affording a new carbocation with the positively charged carbon atom of the carbocyclic fragment. The stabilization of such electrophilic species occurs through the successive interactions first with the solvent molecule (acetonitrile) with the formation of intermediate imino cation which reacts with a second phosphine molecule [scheme (1)].

The reaction of carbocations with acetonitrile are fairly frequent, the events of this electrochemical interaction have been described in [3]. The end products are different acetamides formed under the action of water. In our experimental conditions (water-free electrolyte) we first succeeded in isolating a stable compound, the phosphonioimine **I**. Interestingly, earlier in the study of reactions of anodically generated cation radicals of the organophosphorus compounds the products of interaction with acetonitrile were not detected [4]. Note an unexpected (and not yet



(1)

explained) selectivity of the studied process, namely, thesequential interaction of the carbocation with a molecule of acetonitrile and only after that with the original phosphine.

When carrying out experiments of growing crystals, we found that in time changes were observed in the ^{31}P NMR spectrum of compound **I**: The relative intensity of the signal δ_P 31.7 ppm gradual decreased while simultaneously a doublet signal in the region 12 ppm appeared belonging to the protonated tripropylphosphine. We succeeded to isolate a crystalline sample of the new compounds (δ_P 34.3 ppm) by slow precipitation from acetonitrile at cooling. The

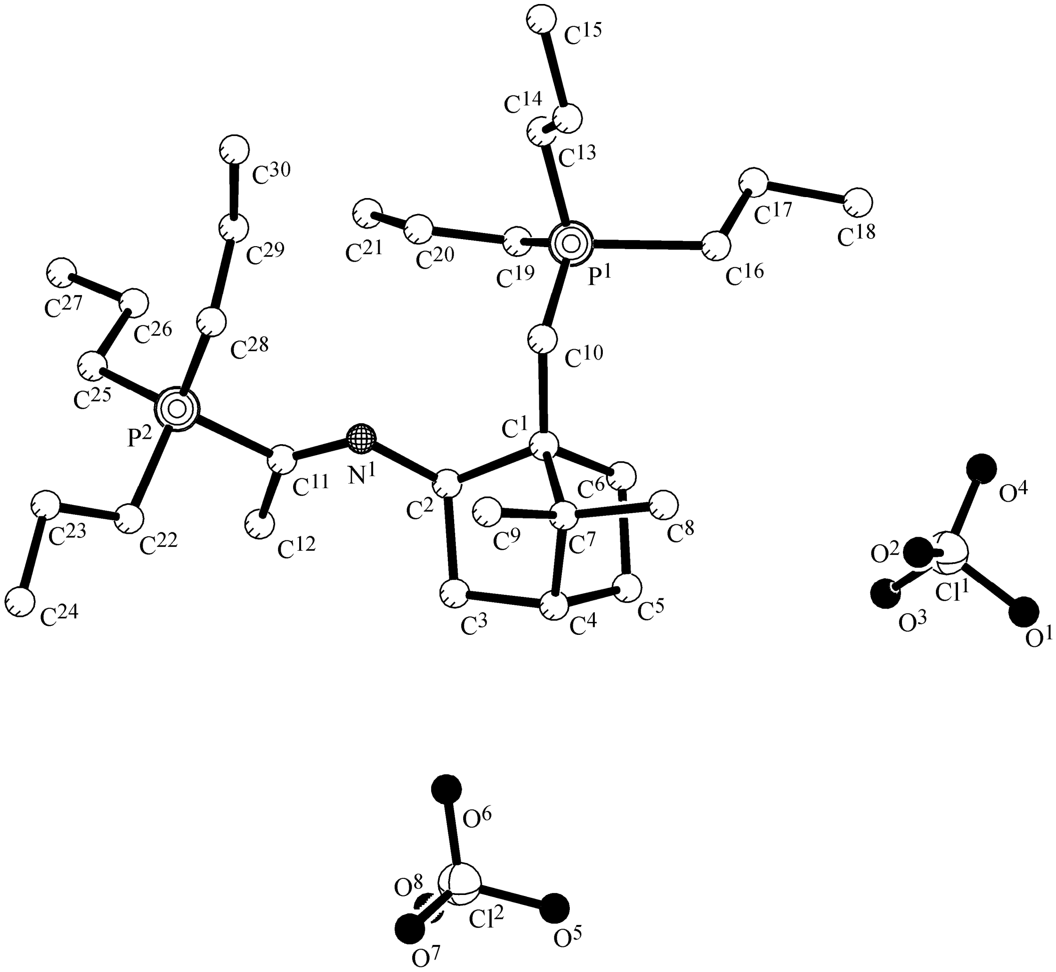


Fig. 1. The geometry of the cationic and anionic fragments of compound **I** in the crystal (without hydrogen atoms).

Geometrical parameters [bond lengths (Å) and bond angles (deg)] of compounds **I** and **II**

Bond, angle	**I**	**II**	Angle	**I**	**II**
C^1–C^2	1.566(6)	1.579(7)	$C^1C^7C^9$	114.8(5)	114.5(6)
C^1–C^6	1.536(7)	1.555(8)	$C^1C^{10}P^1$	122.3(4)	120.5(4)
C^1–C^7	1.572(8)	1.541(9)	$C^2C^1C^6$	104.4(4)	103.2(4)
C^1–C^{10}	1.538(6)	1.553(7)	$C^2C^1C^7$	103.6(4)	104.2(4)
C^2–N^1	1.452(6)	1.455(8)	$C^2C^1C^{10}$	115.1(3)	115.8(4)
C^2–C^3	1.550(7)	1.567(10)	$C^2C^3C^4$	103.8(5)	103.5(5)
C^3–C^4	1.512(9)	1.513(11)	$C^2N^1C^{11}$	118.3(4)	121.7(4)
C^4–C^5	1.503(11)	1.555(10)	$C^3C^2N^1$	114.3(4)	116.3(5)
C^4–C^7	1.570(9)	1.541(10)	$C^3C^4C^5$	108.0(6)	108.4(6)
C^5–C^6	1.563(8)	1.559(10)	$C^3C^4C^7$	103.2(5)	103.7(6)
C^7–C^8	1.517(9)	1.532(10)	$C^4C^5C^6$	102.5(5)	102.0(6)
C^7–C^9	1.557(10)	1.525(10)	$C^4C^7C^8$	113.5(5)	114.4(6)
C^{10}–P^1	1.777(5)	1.799(6)	$C^4C^7C^9$	114.0(6)	112.9(6)
C^{11}–C^{12}	1.512(8)	1.520(10)	$C^5C^4C^7$	104.2(5)	102.1(6)
C^{11}–N^1	1.242(6)	1.328(8)	$C^6C^1C^7$	102.1(4)	101.7(5)
C^{11}–P^2	1.830(6)		$C^6C^1C^{10}$	117.7(4)	115.1(4)
C^{11}–O^{11}		1.245(7)	$C^7C^1C^{10}$	112.3(4)	115.1(5)
C^{13}–C^{14}	1.398(12)	1.534(9)	$C^8C^7C^9$	108.7(6)	106.7(6)
C^{13}–P^1	1.825(8)	1.819(7)	$C^{10}P^1C^{13}$	106.8(3)	106.6(3)
C^{14}–C^{15}	1.507(14)	1.463(11)	$C^{10}P^1C^{16}$	104.7(3)	112.4(3)
C^{16}–C^{17}	1.444(14)	1.512(10)	$C^{10}P^1C^{19}$	118.7(3)	113.3(3)
C^{16}–P^1	2.009(9)	1.821(7)	$C^{11}P^2C^{22}$	101.1(3)	
C^{17}–C^{18}	1.469(14)	1.492(11)	$C^{11}P^2C^{25}$	109.2(3)	
C^{19}–C^{20}	1.383(11)	1.525(10)	$C^{11}P^2C^{28}$	111.8(3)	
C^{19}–P^1	1.731(7)	1.779(7)	$C^{12}C^{11}N^1$	129.2(5)	118.9(5)
C^{20}–C^{21}	1.663(11)	1.533(10)	$C^{12}C^{11}P^2$	115.8(4)	
C^{22}–C^{23}	1.418(12)		$C^{13}C^{14}C^{15}$	112.3(8)	114.0(6)
C^{22}–P^2	1.879(8)		$C^{13}P^1C^{16}$	105.6(3)	107.5(3)
C^{23}–C^{24}	1.495(13)		$C^{13}P^1C^{19}$	108.6(3)	107.7(3)
C^{25}–C^{26}	1.492(11)		$C^{14}C^{13}P^1$	120.8(6)	116.5(4)
C^{25}–P^2	1.783(7)		$C^{16}C^{17}C^{18}$	102.6(8)	113.2(6)
C^{26}–C^{27}	1.517(13)		$C^{16}P^1C^{19}$	111.6(4)	109.0(3)
C^{28}–C^{29}	1.420(12)		$C^{17}C^{16}P^1$	113.6(6)	115.3(5)
C^{28}–P^2	1.771(7)		$C^{19}C^{20}C^{21}$	113.6(6)	111.1(6)
C^{29}–C^{30}	1.577(13)		$C^{20}C^{19}P^1$	113.2(5)	116.1(5)
Cl^1–O^1	1.348(10)	1.359(6)	$C^{22}C^{23}C^{24}$	106.6(8)	
Cl^1–O^2	1.270(9)	1.372(10)	$C^{22}P^2C^{25}$	110.6(3)	
Cl^1–O^3	1.317(7)	1.364(8)	$C^{22}P^2C^{28}$	109.3(3)	
Cl^1–O^4	1.338(7)	1.327(13)	$C^{23}C^{22}P^2$	116.6(7)	
Cl^2–O^5	1.363(7)		$C^{25}C^{26}C^{27}$	114.1(7)	
Cl^2–O^6	1.362(8)		$C^{25}P^2C^{28}$	114.2(3)	
Cl^2–O^7	1.343(12)		$C^{26}C^{25}P^2$	115.2(5)	
Cl^2–O^8	1.317(13)		$C^{28}C^{29}C^{30}$	113.6(8)	
$C^1C^2C^3$	102.1(4)	101.6(5)	$C^{29}C^{28}P^2$	117.6(6)	
$C^1C^2N^1$	114.2(4)	116.0(4)	$N^1C^{11}P^2$	115.0(4)	
$C^1C^6C^5$	103.4(4)	103.5(5)	$C^2N^1H^1$		120.00
$C^1C^7C^4$	91.1(5)	93.5(5)	$C^{11}N^1H^1$		117.00

(Contd.)

Bond, angle	I	II	Angle	I	II
$C^1C^7C^8$	114.0(5)	114.8(5)	$C^{12}C^{11}O^{11}$		118.8(5)
$N^1C^{11}O^{11}$		122.2(5)	$O^5Cl^2O^6$	110.3(5)	
$O^1Cl^1O^2$	102.5(12)	113.1(5)	$O^5Cl^2O^7$	107.7(7)	
$O^1Cl^1O^3$	105.5(6)	114.2(4)	$O^5Cl^2O^8$	110.1(6)	
$O^1Cl^1O^4$	105.1(7)	107.4(7)	$O^6Cl^2O^7$	102.5(7)	
$O^2Cl^1O^3$	113.9(6)	112.6(6)	$O^6Cl^2O^8$	114.3(5)	
$O^2Cl^1O^4$	114.7(8)	98.0(7)	$O^7Cl^2O^8$	111.6(9)	
$O^3Cl^1O^4$	113.6(5)	110.3(6)			

geometry of the molecule of this substance is shown in Fig. 2. As seen, this compound is 2-acetamido-10-tripropylphosphobornane perchlorate (**II**). The crystal structure of compound **II** was solved, like that of crystal **I**, in the space group $P2_1/n$. Geometric parameters (bond lengths and bond angles) of **II** are listed in table.

Reaction of the formation of 2-acetamido-10-tripropylphosphoniobornane perchlorate (taking into account the release of protonated phosphine in the course of the process as established by ^{31}P NMR spectroscopy) can be described by the scheme (2).

It was indicated [5] that in the hydrolysis of phosphonium salts with acceptor functional groups (in particular, an imino group), the attack by a nucleophile on the α-carbon was not characteristic, and almost always it was directed on the phosphorus atom with the formation of phosphine oxides. Unusual course of the reaction of hydrolysis of the diphosphonioiminobornane is probably due to the joint action of the following factors: (1) the steric overloading of the phosphorus atom P^2, and therefore greater availability to attack by the water oxygen atom of partially positively charged (because of the strong negative inductive effect of the phosphonium group) sp^2

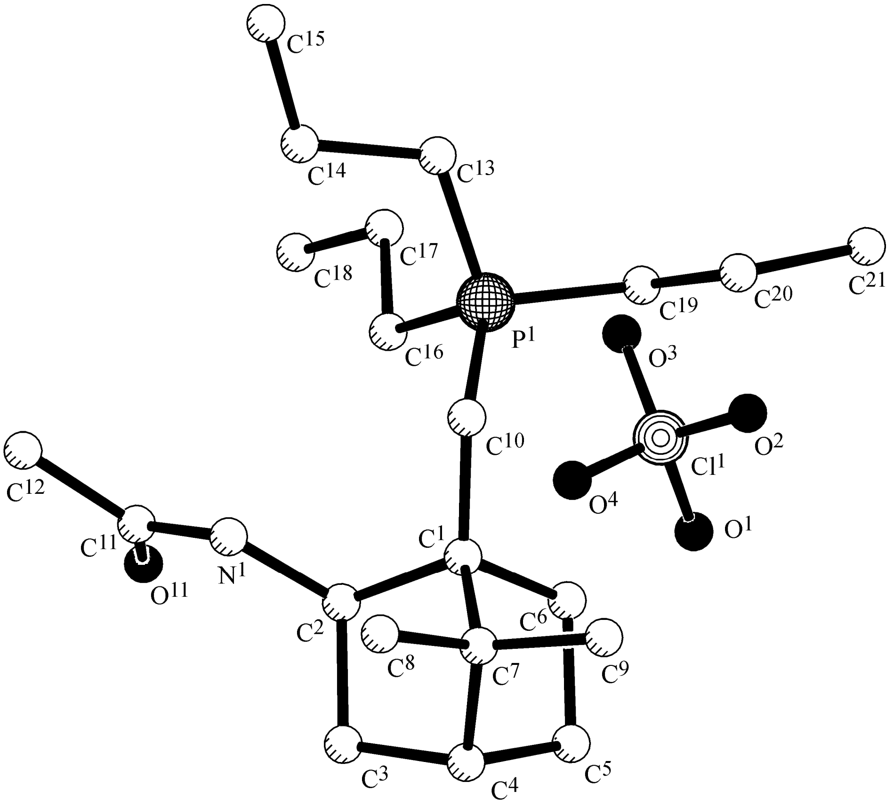
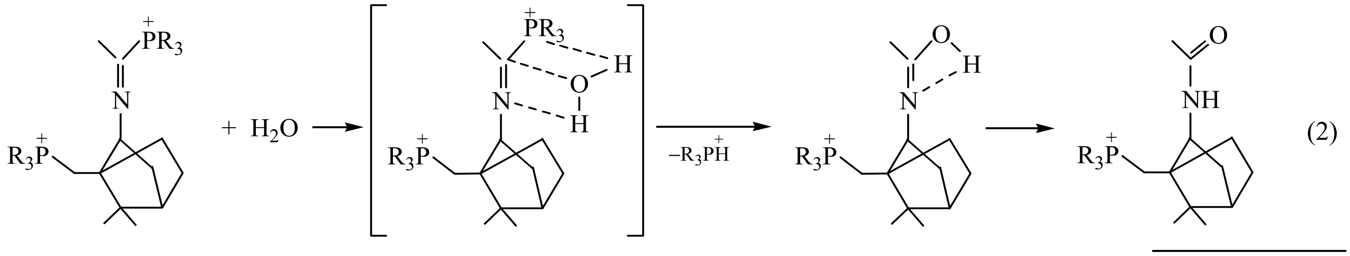


Fig. 2. The geometry of the cation-anion pair of compound **II** in the crystal (without hydrogen atoms).



hybridized carbon atom of imine fragment (C^{11}), (2) a large electronegativity of the nitrogen atom N^1, which forms a hydrogen bond with the proton of the water molecule. One can assume that at the interaction of water with diphosphonioiminobornane a six-membered transition state is formed [scheme (2)].

According to XRD analysis (see table), the functional groups (phosphonium and iminophosphonium) did not affect significantly the bornane geometry. The bond lengths of carbon atoms in the bornane ring are in the range 1.50–1.58 Å, and the values of bond angles in the region of 101°–108°, except for the bond angles at the C^7 atom [the $C^1C^7C^4$ angle is approximately 90°, $C^1(C^4)C^7C^8(C^9)$ angles are approximately 114°]. The close the geometric parameters of the bornane rings in compounds **I** and **II** should be mentioned. The imine multiple bond geometry in **I** is normal, with virtually no distortion. Unshared electron pair of the nitrogen atom is in the *cis* position relative to the phosphonium group. Phosphonium groups have a common structure: The phosphorus atom has the tetrahedral coordination, a sterically favorable *twist* conformation is observed along the P–C_{sp^3} bonds, the P^1–C_{sp^3} bond lengths are in the range 1.73–1.83 Å, except for the somewhat elongated P^1–C^{16} bond (2.01 Å) in compound **I**. In the crystal of compound **II** the formation of the classical NH···O hydrogen bonds is observed joining the molecules of the same chirality to form the zigzag chains along the 2_1 axis. Parameters of hydrogen bonds are shown below.

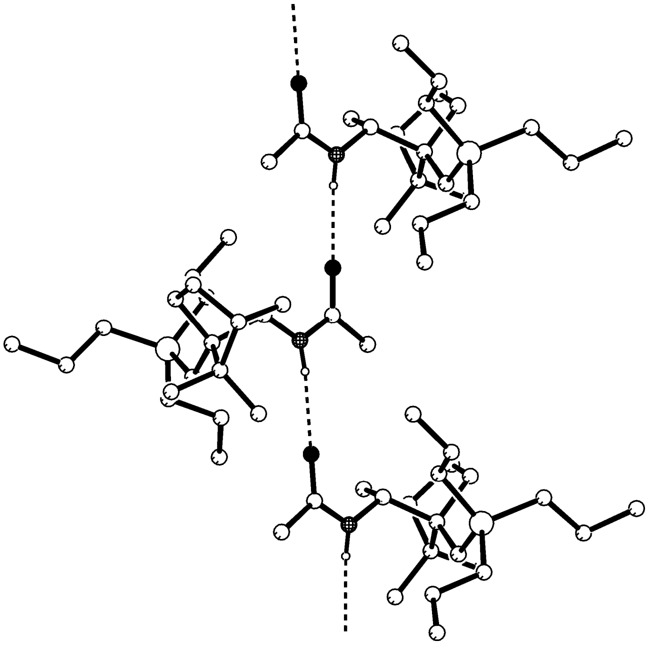


Fig. 3. Hydrogen-bonded chain of molecules in the crystal of **II** along *c* axis.

Bond	N^1–H···O^{11}
Symmetry transformation	$1/2 - x, -1/2 + y, 1/2 - z$
N–H, Å	0.8300
H···O, Å	2.290
N···O, Å	3.062(6)
∠N–H···O, deg	154.00

Thus, it was found that among the products of the electrochemical oxidation of tertiary phosphines in the presence of camphene there are diphosphonioiminobornanes resulting from rearrangement of the intermediate dication by the Wagner–Meerveyn mechanism [6]. The hydrolysis of these bornyldiphosphonium perchlorates leads to the synthesis of 2-acetamido-10-phosphoniobornane.

EXPERIMENTAL

The electrochemical synthesis technique and the procedure for the preparative chromatographic separation of the diperhlorate **I** was described in [2]. This compound was crystallized from a solution in methanol. The melting point of the crystalline sample **I** is 173–176°C. 2-Acetamidoyl-10-(tripropylphosphonium)methylnorbornane **II** was separated from the compound **I** by precipitation with chloroform. Colorless crystals of **II** were grown from acetonitrile solution by slow cooling. The melting temperature of the crystalline sample of **II** is 180–182°C.

The XRD study of crystals was carried out on a Bruker SMART Apex II diffractometer (graphite monochromator, $\lambda MoK_\alpha = 0.71073$ Å). The accounting for extinction was performed semiempirically with the SADABS software [7]. The structure was solved by the direct method with SHELXS software [8]. The positions of nonhydrogen atoms were refined in the isotropic and then anisotropic approximations with the SHELXL-97 software [9]. Hydrogen atoms not involved in hydrogen bonding were placed in calculated positions and refined using the *rider* model. The amino group hydrogen atom in the structure of **II** was revealed from the difference Fourier series, and refined isotropically in the final stage. All calculations were performed using the WinGX [10] and APEX2 software [11]. Drawings were made using the PLATON software [12].The XRD data of structures **I** and **II** are deposited in the Cambridge Structural Database (registration number 880583 and 880584, respectively). The crystals of compound **I** are monoclinic; $(C_{30}H_{61}NP_2)^{2+}\cdot 2ClO_4^-$, at 20°C: $a = 17.580(9)$, $b = 10.258(5)$, $c = 21.257(11)$ Å, $\beta = 103.176(6)°$, $V = 3733(3)$ Å^3, $Z = 4$, $d_{calc} = 1.240$ g cm^{-3}, space group $P2_1/n$, μMo 3.4 cm^{-1}. We measured the intensity of 7255 independent reflections, 4239 of which with $I \geq 2\sigma$. The final values of divergence factors $R = 0.1101$, $R_W = 0.3686$. The crystals of compound **II** are monoclinic; $(C_{21}H_{41}NP)^+\cdot ClO_4^-$ at 20°C: $a = 10.770(5)$, $b = 9.752(5)$, $c = 24.364(11)$ Å, $\beta = 97.214(6)°$, $V = 2539(2)$ Å^3, $Z = 4$, $d_{calc} = 1.188$ g cm^{-3}, space group $P2_1/n$, μMo = 2.42 cm^{-1}. We measured the intensity of 5501 independent reflections, 2339 of which with $I \geq 2\sigma$. The final values of divergence factors $R = 0.1204$, $R_W = 0.3639$.

ACKNOWLEDGMENTS

We are grateful to Russian Ministry of Education for financial suport (state contract no. 16.552.11.7008).

REFERENCES

1. Zagumennov, V.A., Sizova, N.A., and Nikitin, E.V., *Zh. Obshch, Khim*., 2009, vol. 79, no. 7, p. 1116.
2. Zagumennov, V.A. and Sizova, N.A., *Zh. Obshch, Khim*., 2012, vol. 82, no. 8, p. 1288.
3. *Organic Electrochemistry*, Petrosyan, V.A. and Feoktistov, L.G., Eds., Moscow: Khimiya, 1983.
4. Zagumennov, V.A. and Nikitin, E.V., *Russ. Khim. Zh*., 2005, vol. 49, no. 5, p. 49.
5. Erastov, O.A. and Nikonov, G.N., *Functionally Phosphines and Their Derivatives*, Moscow: Nauka, 1986, p. 140.
6. Plemenkov, V.V., *Introduction to the Chemistry of Natural Compounds*, Kazan, 2001.
7. Sheldrick, G.M., *SADABS* , Germany, University of Göttingen, 2004.
8. Sheldrick, G.M., *Acta Crystal., Sec. A*., 2008, vol. 64, no. 1, p. 112.
9. Sheldrick, G.M., *SHELXL-97*, Germany, University of Goettingen, 1997.
10. Farrugia, L.J., J. *Appl. Crystall*., 1999, vol. 32, no. 4, p. 837.
11. *APEX2 (Version 2.1), SAINTPlus. Version 7.31A. Bruker Advansed X-ray Solutions*, BrukerAXS Inc., USA, Madison, Wisconsin, 2006.
12. Spek, A.L., *J. Appl. Crystall.,* 2003, vol. 36, no. 1, p. 7.