ISSN 1070-3632, Russian Journal of General Chemistry, 2011, Vol. 81, No. 2, pp. 429–430. © Pleiades Publishing, Ltd., 2011.
Original Russian Text © L.K. Kibardina, S.A. Terent'eva, A.R. Burilov, M.A. Pudovik, 2011, published in Zhurnal Obshchei Khimii, 2011, Vol. 81, No. 2, pp. 331–332.

LETTERS TO THE EDITOR

Salt Structures in a Series of Hexacoordinated Phosphorus Polycyclic Derivatives

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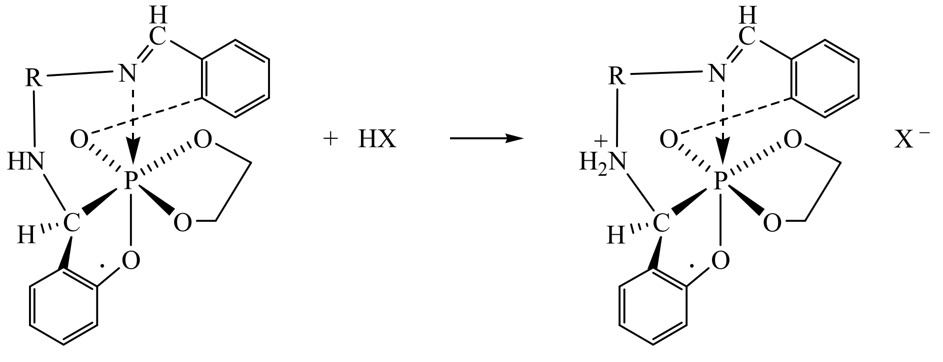
Received July 20, 2010

DOI: 10.1134/S1070363211020277

Recently we synthesized polycyclic framework structures of new type formed via the nitrogen–phosphorus intramolecular coordination bonding [1]. The presence of a secondary amino group connected with the phosphorus atom through a carbon atom (aminoalkylphosphonate analog) determines a possibility to form a salt structure on this basis. Compounds **Ia–Id** were found to react with dibromoacetic and picric acids in a solvent at room temperature to afford the compounds of salt structure **IIa–IId**. The chemical shift of the phosphorus atom is observed in the range of –113 to –116 ppm, which is characteristic of the compounds of the hexacoordinated phosphorus atom.



Ia, Ib **IIa–IId**

Ia, R = cyclohexyl; **Ib,** R = $(CH_2)_2$; **IIa** R = cyclohexyl, X^- = $CHBr_2C(O)O$; **IIb,** R = cyclohexyl, X = 2,4,6-$(NO_2)_3C_6H_2O$; **IIc,** R = $(CH_2)_2$, X^- = $CHBr_2C(O)O$; **IId,** R = $(CH_2)_2$, X = 2,4,6-$(NO_2)_3C_6H_2O$.

The structure of compounds obtained was confirmed by the ^1H, ^{31}P NMR, IR spectroscopy, and composition, by the elemental analysis. Due to the salt structure, in the ^1H spectra the protons of these compounds appear as poorly resolved broad signals. Therefore only a group analysis can be made based on the chemical shifts without considering their fine structure. The compounds obtained undergo changes at prolonged contact with air.

1,1-Ethylenedioxy-3,4,11,12-dibenzo-6-aza-7,8-tetramethyleno-9-ammonia-2,13-dioxa-1-phospha [8.3.0^{1,10}]tridecatri-3,5,11-ene dibromoacetate (IIa). A solution of 0.41 g of compound **Ia** and 0.22 g of dibromoacetic acid in 5 ml of methylene chloride was maintained for 6 h at 20°C. The target product was precipitated from ether. Yield 0.40 g (64%), mp 116°C. IR spectrum (KBr), ν, cm^{-1} 33 (C=N), 1732 [C(O)O], 2580–2700 (NH_2^+). ^{31}P NMR spectrum ($CDCl_3$), δ_P, ppm: –114.29. Found, %: Br 25.63; N 4.59; P 4.79. $C_{24}H_{27}Br_2N_2O_6P$. Calculated, %: Br 25.39; N 4.44; P 4.92.

1,1-Ethylenedioxy-3,4,11,12-dibenzo-6-aza-7,8-tetramethyleno-9-ammonia-2,13-dioxa-1-phospha [8.3.0^{1,10}]tridecatri-3,5,11-ene picrate (IIb) was prepared similarly from 0.41 g of compound **Ia** and 0.23 g of picric acid. Yield 0.3 g (47%), mp 170–174°C. IR spectrum (KBr), ν, cm^{-1}: 1633 (C=N), 2490–2854 (NH_2^+). ^{31}P NMR spectrum ($CDCl_3$), δ_P, ppm: –113.96. Found, %: N 10.95; P 4.93. $C_{28}H_{28}N_5O_{11}P$. Calculated, %: N 10.92; P 4.83.

1,1-Ethylenedioxy-3,4,11,12-dibenzo-6-aza-9-ammonia-2,13-dioxa-1-phospha[8.3.0^{1,10}]tridecatri-3,5,11-ene dibromoacetate (IIc) was prepared similarly from 0.36 g of compound **Ib** and 0.22 g of dibromoacetic acid. Yield 0.31 g (53%), mp 214–218°C. IR spectrum (KBr), ν, cm^{-1}: 1628 (C=N), 1734 [C(O)O], 2480–2856 (NH_2^+). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 3.42–3.47 m (2H), 3.48–3.54 m (2H), 3.69–3.74 m (1H), 3.77–3.79 m (1H), 3.96–4.02 m (1H), 4.32–4.38 m (1H), 4.48–4.55 m (1H), 6.81–7.75 m (8H). ^{31}P NMR spectrum ($CDCl_3$), δ_P, ppm: –116.66. Found, %: Br 27.21; P 5.87. $C_{20}H_{21}Br_2N_2O_6P$. Calculated, %: Br 27.77; P 5.38.

1,1-Ethylenedioxy-3,4,11,12-dibenzo-6-aza-9-ammonia-2,13-dioxa-1-phospha[8.3.0^{1,10}]tridecatri-3,5,11-ene picrate (IId) was prepared similarly from 0.36 g of compound **Ib** and 0.23 g of picric acid. Yield 0.40 g (69%), mp 102–106°C. IR spectrum (KBr), ν, cm^{-1}: 1630 (C=N), 2480–2857 (NH_2^+). ^{31}P NMR spectrum ($CDCl_3$), δ_P, ppm: –115.91. Found, %: N 11.45; P 4.87. $C_{24}H_{22}N_5O_{11}P$. Calculated, %: N 11.92; P 5.28.

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