ISSN 1070-3632, Russian Journal of General Chemistry, 2010, Vol. 80, No. 2, pp. 366–367. © Pleiades Publishing, Ltd., 2010.
Original Russian Text © R.Kh. Bagautdinova, L.K. Kibardina, A.R. Burilov, M.A. Pudovik, 2010, published in Zhurnal Obshchei Khimii, 2010, Vol. 80, No. 2, pp. 339–340.

LETTERS
TO THE EDITOR

Reaction of Salicylalkylenediimines with 2-Chloro-4,5-diphenyl-1,3,2-dioxaphospholene

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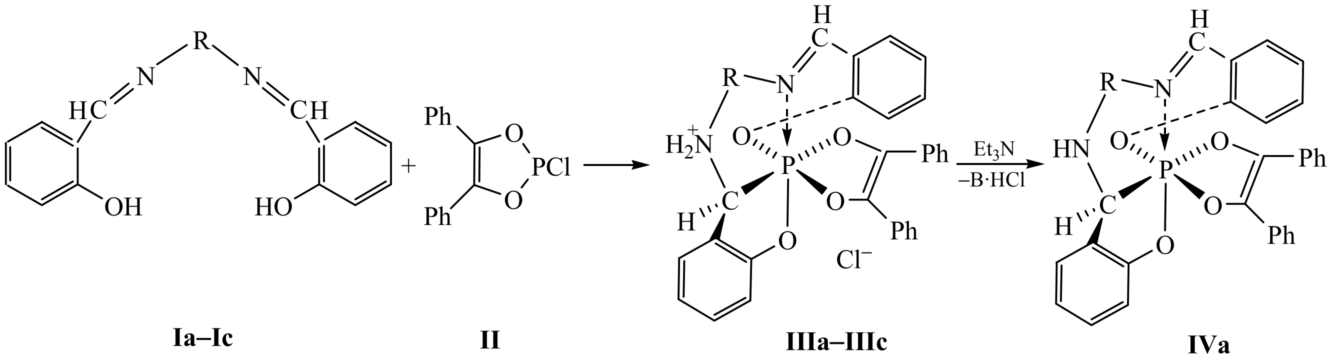
Received July 9, 2009

DOI: 10.1134/S1070363210020313

Reaction of salicyl(cyclo)alkylenediimine **Ia–Ic** with 4,5-diphenyl-2-chloro-1,3,2-dioxaphospholene **II** was found to occur as a cascade cyclization giving rise to tetracyclic derivatives **IIIa–IIIc** of the hexacoordinated phosphorus atom of the salt structure involving intramolecular transannular N→P bond.



I, III, IV: R = $(CH_2)_2$ (**a**); $(CH_2)_3$ (**b**); cyclohexyl (**c**).

The structure of compounds **IIIa–IIIc** was proved by the IR, ^{1}H, and ^{31}P NMR spectroscopy, mass spectrometry, and composition, by the elemental analysis data. The IR spectra of the products **IIIa–IIIc** contain absorption bands at 1623–1627 (C=N) and 2590–2724 cm^{-1} (broadened complex band, NH_2^+). The chemical shift of the phosphorus atom at δ_P from –114 to –122 ppm is characteristic of the hexacoordinated phosphorus derivatives. Notice that the ^{31}P NMR spectra of the reaction mixtures of **IIIa–IIIc** contain signals indicative of the formation of diastereoisomers mixture. As a result of fractional crystallization compound **IIIa** was obtained as the two diastereoisomers mixture in the ratio 1:1. Compounds **IIIb** and **IIIc** were isolated as individual diastereomers. Due to their salt structure the ^{1}H NMR spectra of compounds **IIIa–IIIc** contain poorly resolved signals, therefore only group analysis of the proton signals was performed on the basis of chemical shifts without considering the fine structure of the spectra. The transannular N→P bond (2.006–2.007 Å) is realized in the compounds **IIIa–IIIc**. The intermolecular bonding of similar type was earlier observed in the series of pentacoordinated phosphorus derivatives [1–5]. On treating with triethylamine, the product **IIIa** undergoes dehydrochlorination to give phosphorate **IVa** of neutral structure (δ_P –105.87 ppm).

1,1-Diphenylethenedioxy-3,4,11,12-dibenzo-6-aza-9-ammonia-2,13-dioxa-1-phospha[8.3.0^{1,10}]tridecatri-3,5,11-ene chloride (IIIa). To a solution of 1.13 g of salicylethylenediimine **Ia** in 10 ml of anhydrous methylene chloride was added dropwise 1.17 g of chloroderivative **II.** After 24 h the precipitate was separated and washed with diethyl ether. Yield 1.88 g (82%), light brown powder, mp 165–167°C. IR spectrum, ν, cm^{-1}: 1607 (Ph), 1627 (C=N), 2597, 2669 (NH_2^+). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.02 br.s (2H, NH_2^+), 3.20–3.37 m (1H, CH_2), 3.60 d (1H, CH_2, $^2J_{HH}$ 12.29 Hz), 3.77 d (1H, CH_2, $^2J_{HH}$ 10.25 Hz), 4.10–4.50 m (1H, CH_2), 4.73 s (1H, PCH), 6.86–7.69 m (18H, Ph), 8.32 br.s (1H, N=CH). ^{31}P NMR spectrum (DMSO-d_6), δ_P, ppm: from –115.98 to –122.60 (1:1). Mass spectrum (MALDI–TOF), *m*/*z*: 507 [M^+ – HCl]. Found, %: C 66.44; H 4.92; Cl 6.36; N 5.36; P 5.46. $C_{30}H_{26}ClN_2O_4P$. Calculated, %: C 66.11; H 4.82; Cl 16.50; N 5.36; P 5.68.

1,1-Diphenylethenedioxy-3,4,11,12-dibenzo-6-aza-10-ammonia-2,14-dioxa-1-phospha[9.3.0^{1,11}]tridecatri-3,5,12-ene chloride (IIIb). To a solution of 1.23 g of salicylpropylenediimine **Ib** in 10 ml of anhydrous methylene chloride was added dropwise 1.21 g of chloroderivative **II.** After 2 days to this reaction mixture was added 5 ml of anhydrous diethyl ether. The precipitate was separated and washed with diethyl ether. Yield 2.0 g (82%), light brown powder, mp 149–151°C. IR spectrum, ν, cm^{-1}: 1626 (C=N), 2724 (NH_2^+). ^{31}P NMR spectrum ($CDCl_3$), δ_P, ppm: –120.98. Mass spectrum (MALDI–TOF), *m*/*z*: 521 [M^+ – HCl]. Found, %: C 66.41; H 5.44; Cl 6.54; N 5.12; P 5.46. $C_{31}H_{28}ClN_2O_4P$. Calculated, %: C 66.59; H 5.66; Cl 6.34; N 5.01; P 5.54.

1,1-Diphenylethenedioxy-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 chloride (IIIc) was prepared similarly from 1.0 g of salicylcyclohexyldiimine **Ic** and 0.86 g of chloroderivative **II.** Yield 1.4 g (75%), light brown powder, mp 153.5–154°C. IR spectrum, ν, cm^{-1}: 1623 (C=N), 2667 (NH_2^+). ^{31}P NMR spectrum ($CDCl_3$), δ_P, ppm: –105.87. Mass spectrum (MALDI–TOF), *m*/*z*: 561 [M^+ – HCl]. Found, %: C 67.96; H 5.36; Cl 5.93; N 4.76; P 5.06. $C_{34}H_{32}ClN_2O_4P$. Calculated, %: C 68.16; H 5.39; Cl 5.92; N 4.68; P 5.17.

1,1-Diphenylethenedioxy-3,4,11,12-dibenzo-6-aza-9-ammonia-2,13-dioxa-1-phospha[8.3.0^{1,10}]tridecatri-3,5,11-ene (IV). To a suspension of 0.6 g of compound **Ia** in 5 ml of anhydrous methylene chloride was added dropwise 0.2 g of triethylamine. After 5 days the reaction mixture was concentrated and mixed with a small amount of anhydrous diethyl ether. The precipitate was filtered off and washed with water to remove triethylamine hydrochloride. Yield 0.43 g (74%), mp 196–198°C. IR spectrum, ν, cm^{-1}: 1625 (C=N), 3398 (NH). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.11–4.51 m (4H, NCH_2), 6.94–7.28 m (18H, Ph), 7.57 d. d (1H, PCH, $^2J_{PH}$ = $^2J_{HH}$ 7.62 Hz), 8.20 d (1H, NCH, $^2J_{HH}$ 4.12 Hz). ^{31}P NMR spectrum ($CDCl_3$), δ_P, ppm: –105.87. Found, %: N 5.73; P 5.97. $C_{30}H_{25}N_2O_4P$. Calculated, %: N 5.51; P 6.10.

The IR spectra were recorded on a Vector-22 (Bruker) spectrometer in the range of 400–3600 cm^{-1} from mulls in mineral oil. The ^{1}H NMR spectra were registered on a Avance-600 instrument (600.13 MHz) relative to signals of the residual protons of deuterated solvent (chloroform-*d*). The ^{31}P NMR spectra were taken on a Bruker MSL-400 NMR-Fourier spectrometer (100.62 MHz). The mass spectra MALDI–TOF were obtained on a ULTRAFLEX III instrument (matrix *p*-nitroaniline).

ACKNOWLEDGMENTS

This work was financially supported by the Russian Foundation for Basic Research (grant no. 08-03-00029).

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