ISSN 1070-3632, Russian Journal of General Chemistry, 2010, Vol. 80, No. 1, pp. 155–157. © Pleiades Publishing, Ltd., 2010.
Original Russian Text © A.A. Prishchenko, M.V. Livantsov, O.P. Novikova, L.I. Livantsova, E.R. Milayeva, 2010, published in Zhurnal Obshchei Khimii, 2010, Vol. 80, No. 1, pp. 160–162.

LETTERS TO THE EDITOR

Synthesis of Diphosphorus-Substituted Bisamides of Iso- and Terephthalic Acids Containing PCHNC(O) Fragments

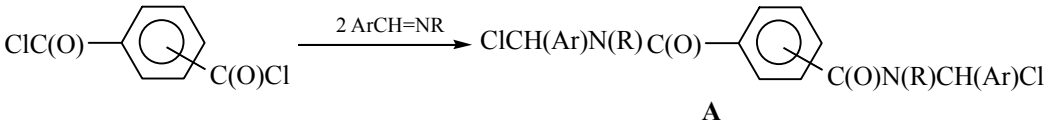
A. A. Prishchenko, M. V. Livantsov, O. P. Novikova, L. I. Livantsova, and E. R. Milayeva

Moscow State University, Vorob'evy gory 1, Moscow, 119992 Russia
e-mail: aprishchenko@yandex.ru

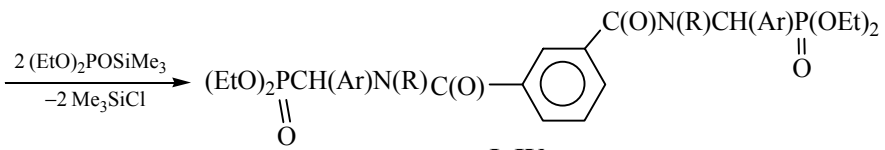
Received June 4, 2009

DOI: 10.1134/S1070363210010263

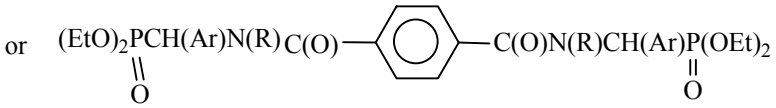
The phosphorus-substituted amides of carboxylic acids are of great interest as effective ligands and biologically active substances of different action [1]. Recently we suggested convenient methods of synthesis of various phosphorus-substituted amides of carboxylic acids including those containing fragments of 2,6-di-*tert*-butylphenol on the basis of easily available *N*-chloroamides and trimethylsilyl esters of the trivalent phosphorus acids [2]. In this work the easily available iso- and terephthaloyl chlorides [3] are shown to add readily to different imines in the methylene chloride medium to give intermediates **A** (cf. [4]), which react smoothly with diethyl(trimethylsilyl)phosphate excess under mild conditions, producing diphosphorus-substituted bisamides **I–VIII** in high yields.



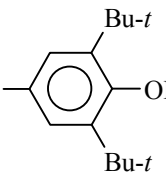
A



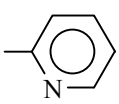
I–IV



V–VIII

Ar = 4-$MeOC_6H_4$ (**I, II, V, VI**), 

(**III, IV, VII, VIII**); R = Me (**I, V**),



(**II, IV, VI, VIII**), Ph (**III, VII**).

The obtained compounds of chelate type **I–VIII** include carbonyl and phosphoryl groups along with the fragments of pyridine and 2,6-di-*tert*-butylphenol. They are of interest as effective polydentate ligands and also as promising antioxidants.

The NMR spectra of compounds **I–VIII** contain characteristic signals of fragments $PC^1HN(C^2)C^3(O)$ whose parameters are given below. In the ^1H and ^{13}C NMR spectra signals of aromatic fragments of these compounds are partially or fully overlapped. Compounds **I–VIII** consist of two stereoisomers. The content of them was determined by the ^1H and ^{31}P NMR spectroscopy. Only the ^{31}P NMR spectra parameters are given for the Second isomers of compounds **III**, **IV**, **VI,** and **VII** due to the low content of these isomers.

1,3-Bis{*N*-methyl-*N*-[4-anisyl(diethoxyphosphoryl)-methyl]aminocarbonyl}benzene (I). To a solution of 6 g of anisal(methyl)amine in 15 ml of methylene chloride was dropwise added 4.06 g of isophthaloyl chloride in 10 ml of methylene chloride at 0°C under stirring. After 1 h to this mixture was added a solution of 8.5 g of diethyl(trimethylsilyl)phosophite in 10 ml of methylene chloride. The mixture was stirred for 2 h at 20°C. The solvent was removed, and to the residue was added 3 ml of hexane. This mixture was cooled to –10°C. The solvent was decanted, and the precipitated crystals were kept in a vacuum of 0.5 mm Hg for 1 h. Yield 12.5 g, 89%, mp 59°C. First isomer, content 75%. ^1H NMR spectrum, δ, ppm: 6.30 d (C^1H, $^2J_{PH}$ 24 Hz), 2.78 s (MeN), 3.59 s (MeO). ^{13}C NMR spectrum, δ, ppm: 52.42 d (C^1, $^1J_{PC}$ 157 Hz), 34.29 (C^2), 170.21 (C^3), 55.03 (MeO), 159.60 ($C_{Ar}O$). ^{31}P NMR spectrum, δ, ppm: 20.50. Second isomer: ^1H NMR spectrum, δ, ppm: 4.92 d (C^1H, $^2J_{PH}$ 24 Hz), 2.69 s (MeN), 3.59 s (MeO). ^{13}C NMR spectrum, δ, ppm: 59.25 d (C^1, $^1J_{PC}$ 155 Hz), 30.81 (C^2), 166.95 (C^3), 55.03 (MeO), 159.60 ($C_{Ar}O$). ^{31}P NMR spectrum, δ, ppm: 20.12. Found, %: C 57.78; H 6.49. $C_{34}H_{46}N_2O_{10}P_2$. Calculated, %: C 57.95; H 6.58.

1,3-Bis{*N*-pyrid-2-yl-*N*-[4-anisyl(diethoxyphosphoryl)methyl]aminocarbonyl}benzene (II). Yield 87%, mp 131°C. First isomer, content 60%. ^1H NMR spectrum, δ, ppm: 5.80 d and 5.82 d (C^1H, $^2J_{PH}$ 20 and 24 Hz), 3.70 s (MeO). ^{13}C NMR spectrum, δ, ppm: 50.61 d (C^1, $^1J_{PC}$ 155 Hz), 172.10 (C^3), 55.48 (MeO). ^{31}P NMR spectrum, δ, ppm: 23.27. Second isomer: ^1H NMR spectrum, δ, ppm: 5.26 d and 5.28 d (C^1H, $^2J_{PH}$ 20 and 24 Hz), 3.70 s (MeO). ^{13}C NMR spectrum, δ, ppm: 58.63 d (C^1, $^1J_{PC}$ 158 Hz), 172.70 (C^3), 55.39 (MeO). ^{31}P NMR spectrum, δ, ppm: 20.74. Found, %: C 60.59; H 5.73. $C_{42}H_{48}N_4O_{10}P_2$. Calculated, %: C 60.72; H 5.82.

1,3-Bis{*N*-phenyl-*N*-[3,5-di-*tert*-butyl-4-hydroxyphenyl(diethoxyphosphoryl)methyl]aminocarbonyl}-benzene (III). Yield 86%, mp 65°C. First isomer, content 95%. ^1H NMR spectrum, δ, ppm: 4.88 d (C^1H, $^2J_{PH}$ 20 Hz), 5.70 br.s (OH), 1.42 s (*t*-Bu). ^{13}C NMR spectrum, δ, ppm: 54.62 d (C^1, $^1J_{PC}$ 151 Hz), 147.97 d (C^2, $^3J_{PC}$ 14 Hz), 165.53 (C^3), 153.62 ($C_{Ar}OH$), 30.33 and 34.87 (*t*-Bu). ^{31}P NMR spectrum, δ, ppm: 23.67. Second isomer: ^{31}P NMR spectrum, δ, ppm: 20.86. Found, %: C 67.81; H 7.54. $C_{58}H_{78}N_2O_{10}P_2$. Calculated, %: C 67.95; H 7.67.

1,3-Bis{*N*-pyrid-2-yl-*N*-[3,5-di-*tert*-butyl-4-hydroxyphenyl(diethoxyphosphoryl)methyl]aminocarbonyl}benzene (IV). Yield 89%, mp 94°C. First isomer, content 95%. ^1H NMR spectrum, δ, ppm: 6.39 d (C^1H, $^2J_{PH}$ 24 Hz), 5.72 br.s (OH), 1.41 s (*t*-Bu). ^{13}C NMR spectrum, δ, ppm: 57.61 d (C^1, $^1J_{PC}$ 159 Hz), 160.46 (C^2), 165.76 (C^3), 154.10 ($C_{Ar}OH$), 30.33 and 34.87 (*t*-Bu). ^{31}P NMR spectrum, δ, ppm: 21.36. Second isomer: ^{31}P NMR spectrum, δ, ppm: 21.80. Found, %: C 65.43; H 7.39. $C_{56}H_{76}N_4O_{10}P_2$. Calculated, %: C 65.48; H 7.46.

1,4-Bis{*N*-methyl-*N*-[4-anisyl(diethoxyphosphoryl)-methyl]aminocarbonyl}benzene (V). Yield 92%, mp 83°C. First isomer, content 80%. ^1H NMR spectrum, δ, ppm: 6.47 d (C^1H, $^2J_{PH}$ 20 Hz), 2.91 s (MeN), 3.81 s (MeO). ^{13}C NMR spec-trum, δ, ppm: 52.52 d (C^1, $^1J_{PC}$ 157 Hz), 34.42 (C^2), 171.19 (C^3), 55.23 (MeO). ^{31}P NMR spectrum, δ, ppm: 23.56. Second isomer: ^1H NMR spectrum, δ, ppm: 4.45 d (C^1H, $^2J_{PH}$ 20 Hz), 2.86 (MeN), 3.78 (MeO). ^{13}C NMR spectrum, δ, ppm: 59.33 d (C^1, $^1J_{PC}$ 156 Hz), 34.78 (C^2), 171.67 (C^3), 55.23 (MeO). ^{31}P NMR spectrum, δ, ppm: 23.84. Found, %: C 57.69; H 6.52. $C_{34}H_{46}N_2O_{10}P_2$. Calculated, %: C 57.95; H 6.58.

1,4-Bis{*N*-pyrid-2-yl-*N*-[4-anisyl(diethoxyphosphoryl)methyl]aminocarbonyl}benzene (VI). Yield 90%, mp 91°C. First isomer, content 95%. ^1H NMR spectrum, δ, ppm: 5.92 d (C^1H, $^2J_{PH}$ 24 Hz), 3.83 s (MeO). ^{13}C NMR spectrum, δ, ppm: 50.66 d (C^1, $^1J_{PC}$ 154 Hz), 157.54 d (C^2, $^3J_{PC}$ 9 Hz), 168.5 s (C^3), 55.13 s (MeO), 159.31 s ($C_{Ar}O$). ^{31}P NMR spectrum, δ, ppm: 23.47. Second isomer: ^{31}P NMR spectrum, δ, ppm: 20.98. Found, %: C 60.64; H 5.74. $C_{42}H_{48}N_4O_{10}P_2$. Calculated, %: C 60.72; H 5.82.

1,4-Bis{*N*-phenyl-*N*-[3,5-di-*tert*-butyl-4-hydroxyphenyl(diethoxyphosphoryl)methyl]aminocarbonyl}benzene (VII). Yield 87%, mp 101°C. First isomer, content 98%. ^{1}H NMR spectrum, δ, ppm: 5.00 d (C^{1}H, $^{2}J_{PH}$ 20 Hz), 5.78 br.s (OH), 1.57 s (*t*-Bu). ^{13}C NMR spectrum, δ, ppm: 60.21 d (C^{1}, $^{1}J_{PC}$ 153 Hz), 147.79 d (C^{2}, $^{3}J_{PC}$ 12 Hz), 169.59 (C^{3}), 153.93 ($C_{Ar}OH$), 34.81 and 30.13 (*t*-Bu). ^{31}P NMR spectrum, δ, ppm: 23.74. Second isomer: ^{31}P NMR spectrum, δ, ppm: 23.05. Found, %: C 67.76; H 7.58. $C_{58}H_{78}N_2O_{10}P_2$. Calculated, %: C 67.95; H 7.67.

1,4-Bis{*N*-pyrid-2-yl-*N*-[3,5-di-*tert*-butyl-4-hydroxyphenyl(diethoxyphosphoryl)methyl]aminocarbonyl}benzene (VIII). Yield 88%, mp 89°C. First isomer, content 65%. ^{1}H NMR spectrum, δ, ppm: 6.40 d (C^{1}H, $^{2}J_{PH}$ 24 Hz), 5.72 br.s (OH), 1.41 s (*t*-Bu). ^{13}C NMR spectrum, δ, ppm: 57.41 d (C^{1}, $^{1}J_{PC}$ 161 Hz), 165.82 (C^{3}), 154.09 ($C_{Ar}OH$), 30.33 and 34.87 (*t*-Bu). ^{31}P NMR spectrum, δ, ppm: 21.28. Second isomer: ^{1}H NMR spectrum, δ, ppm: 6.30 d (C^{1}H, $^{2}J_{PH}$ 24 Hz), 5.72 br.s (OH), 1.41 s (*t*-Bu). ^{13}C NMR spectrum, δ, ppm: 58.08 d (C^{1}, $^{1}J_{PC}$ 160 Hz), 165.59 (C^{3}), 154.09 ($C_{Ar}OH$), 30.33 and 34.87 (*t*-Bu). ^{31}P NMR spectrum, δ, ppm: 21.92. Found, %: C 65.30; H 7.42. $C_{56}H_{76}N_4O_{10}P_2$. Calculated, %: C 65.48; H 7.46.

The NMR spectra were obtained on a Bruker Avance 400 spectrometer using $CDCl_3$ (**I**, **V**) and $(CD_3)_2SO$ (**II–IV**, **VI–VIII**) as solvents and TMS (^{1}H, ^{13}C) and 85% H_3PO_4 in D_2O (^{31}P) as references.

ACKNOWLEDGMENTS

This work was financially supported by the Russian Foundation for Basic Research (grant no. 08-03-00282).

REFERENCES

1. Kolodyazhnyi, O.I., *Usp. Khim*., 2006, vol. 75, no. 3, p. 254.
2. Prishchenko, A.A., Novikova, O.P., Livantsov, M.V., Livantsova, L.I., Koval', Ya.N., and Grigoryev, E.V., *Zh. Obshch. Khim*., 2003, vol. 73, no. 12, p. 2058; Prishchenko, A.A., Livantsov, M.V., Novikova, O.P., Livantsova, L.I., and Milayeva, E.R., *Zh. Obshch. Khim*., 2009, vol. 79, no. 1, p. 156.
3. Oshin, L.A., Treger, Yu.A., Motsarev, G.V., Sonin, E.V., Sergeyev, E.V., Skibinskaya, M.B., and Gol'dfand, E.A., *Promyshlennye khlororganicheskie produkty* (Industrial Organochlorine Products), Moscow: Khimiya, 1978.
4. Achiwa, K. and Sekiya, M., *Chem. Lett*., 1981, no. 9, p. 1213.