ISSN 1070-3632, Russian Journal of General Chemistry, 2009, Vol. 79, No. 4, pp. 864–865. © Pleiades Publishing, Ltd., 2009.
Original Russian Text © O.O. Kolodyazhnaya, O.I. Kolodyazhnyi, 2009, published in Zhurnal Obshchei Khimii, 2009, Vol. 79, No. 4, pp. 691–692.

LETTERS TO THE EDITOR

Reaction in the Ketophosphonate–Triethylphosphite–Diethylchlorophosphite Ternary System

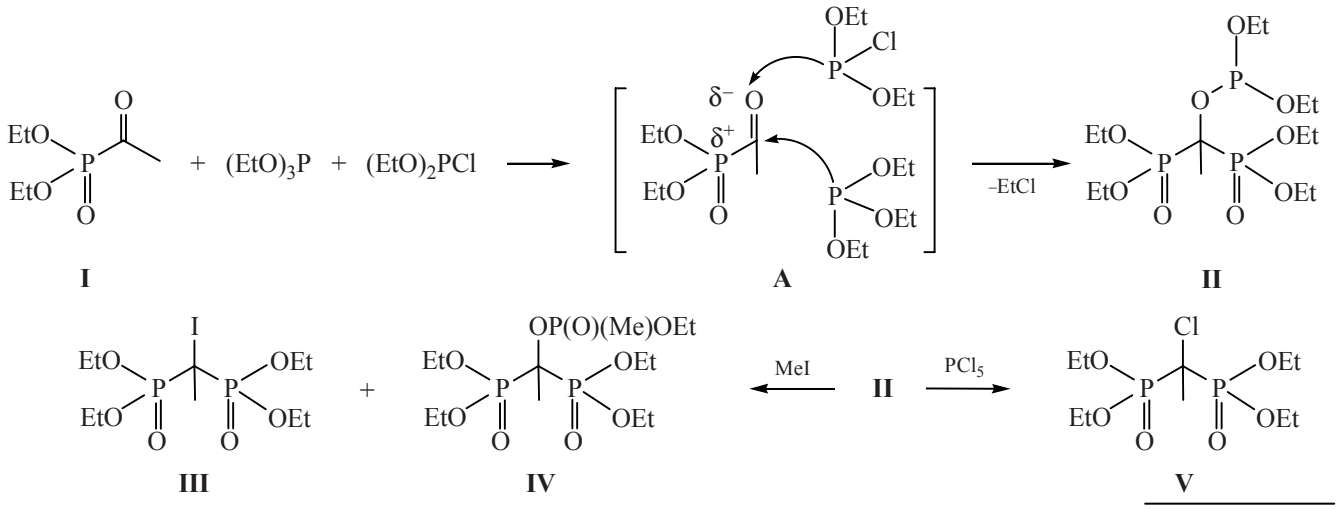
O. O. Kolodyazhnaya and O. I. Kolodyazhnyi

Institute of Bioorganic Chemistry and Petrochemistry, National Academy of Sciences of Ukraine,
ul. Murmanskaya 1, Kiev, 02094 Ukraine
fax: 38(044)573-2555
e-mail: olegkol321@rambler.ru

Received October 16, 2008

DOI: 10.1134/S1070363209040318

We found that reaction of ketophosphonate **I** with triethylphosphite and diethylchlorophosphite proceeds at both carbon atom and carbonyl group oxygen atom to form a new bisphosphonophoshite **II**, which is able to transform into the other bisphosphonate types **III**–**V**. The reaction is an unusual example of simultaneous nucleophilic attack of triethylphosphite and electrophilic attack of diethylchlorophosphite on the polarized carbonyl group as it is shown by the formula of the assumed intermediate **A.**



The reaction of ketophosphonate **I** with triethylphosphite and diethylchlorophosphite occurred with a strong heat evolution and therefore it was carried out with cooling. The reaction gave bisphosphonophosphite **II** in a quantitative yield. This is a viscous oil distillable in a vacuum whose structure was confirmed by ^{1}H and ^{31}P NMR spectroscopy and elemental analysis. In the ^{31}P NMR spectra of **II** two signals at δ_P 134 (the trivalent phosphorus atom) and 18 ppm (the tetracoordinated pentavalent phosphorus atom) were observed with the integral signal ratio 1:2. In the ^{1}H NMR spectra there are signal of methyl group at the methylene carbon atom, triplet with a coupling constant 16 Hz, and also two signals of ethoxy groups at P(III) and P(V) in the ratio 1:2 that confirm the structure of **II**.

Phosphonophosphite **II** enters readily into the Arbuzov reaction yielding the earlier unknown bisphosphonoiodomethane **III** and tris-phosphonate **IV**. We were able to separate these compounds and to purify by vacuum distillation. Reaction of bisphosphonophosphite **II** with phosphorus pentachloride

produces with good yield bis-phosphonochloromethane **V**.

Diethyl 1,1-bis(diethoxyphosphinyl)ethylphosphite (II). A mixture of 0.05 mol of triethylphosphite and 0.05 mol of diethylchlorophosphite was added to 0.05 mol of diethylphosphinomethylketone under stirring and cooling to –20°C. The reaction mixture was kept for 60 min at room temperature. The pure product was isolated by vacuum distillation as colorless oil. Yield 80%, bp 170°C (0.06 mm Hg). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.23 t (6H, C*H*$_3$ [P (III)], $^3J_{HH}$ 7 Hz), 1.32 t (12H, C*H*$_3$ [P(V)], $^3J_{HH}$ 7 Hz), 1.82 t (3H, C*H*$_3$C, $^3J_{HH}$ 16 Hz), 3.88 d. q (4H, CH_2O, $^3J_{HH}$ 7 Hz, $^3J_{PH}$ 3 Hz), 4.17 m (8H, CH_2O). ^{31}P NMR spectrum ($CDCl_3$), δ_P, ppm: 18.1 s [2P, P(V)], 134.2 s [1P, P(III)]. Found, %: C 38.42; H 7.49; P 21.25. $C_{14}H_{33}O_9P_3$. Calculated, %: C 38.36; H 7.59; P 21.20.

The reaction of bis-phosphonophosphite II with methyl iodide. Bis-phosphonophosphite **II,** 0.05 mol, of was mixed with 3 ml of methyliodide at 0°C. The reaction mixture was kept for 12 h. Then methyliodide excess was removed, and residue was distilled in a vacuum. Two fractions were obtained, with bp bp 120°C (0.06 mm Hg) (compound **III**), and with bp 160–170°C (0.06 mm Hg) (compound **IV**).

1,1-Bis(diethoxyphosphinyl)-1-iodomethane (III). Yield 45%, bp 120°C (0.06 mm Hg). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.23 t (6H, C*H*$_3$ [P(III)], $^3J_{HH}$ 7 Hz), 2.0 t (3H, C*H*$_3$, $^3J_{HH}$ 7 Hz), 4.25 m (8H, CH_2O). ^{31}P NMR spectrum ($CDCl_3$), δ_P, ppm: 20.22. Found, %: I 29.75; P 14.53. $C_{10}H_{23}IO_6P_2$ Calculated, %: I 29.64 P 14.47.

Ethyl methyl-[1,1-bis(diethoxyphosphinyl)]ethylphosphonate (IV). Yield 30%, bp 160–170°C (0.06 mm Hg). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.2 t (12H, C*H*$_3$CH$_2$, $^3J_{HH}$ 7 Hz), 1.42 d (3H, C*H*$_3$), 1.55 t (3H, C*H*$_3$C, $^3J_{HH}$ 16 Hz), 4.1 m (2H, CH_2O), 4.2 m (8H, CH_2O). ^{31}P NMR spectrum ($CDCl_3$), δ_P, ppm: 6.26 s (2P, P1), 26.93 s (1P, P2). Found, %: C 36.78; H 7.34; P 21.95. $C_{13}H_{31}O_9P_3$ Calculated, %: C 36.80; H 7.36; P 21.90.

1,1-Bis(diethoxyphosphinyl)-1-chloroethane (V). Yield 60%, bp 100°C (0.06 mm Hg). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.23 t (6H, C*H*$_3$ [P(III)], $^3J_{HH}$ 7 Hz), 1.8 t (3H, C*H*$_3$, $^3J_{HH}$ Hz), 4.25 m (8H, CH_2O). ^{31}P NMR spectrum ($CDCl_3$), δ_P, ppm: 20.22 [4].

The NMR spectra were obtained on a Varian-300 instrument relative to internal TMS (^{1}H and ^{13}C) and to external 85% H_3PO_4 in D_2O (^{31}P).

REFERENCES

1. Bulpin, A., Masson, S., and Sene, A., *Tetrahedron Lett*., 1990, vol. 3l, no. 8, p. 1151.
2. Sturtz, G. and Guervenou, J., *Synthesis,* 1991, no. 8, p. 661.
3. Page, P.C.B., Moore, J.P.G., Mansfield, I., McKenzie, M.J., Bowler, W. B., and Gallagher, J.A., *Tetrahedron*, 2001, vol. 57, no. 7, p. 1837.
4. Seyferth, D. and Marmor, R.S., *J. Organomet. Chem*., 1973, vol. 59, p. 237.