Russian Journal of General Chemistry, Vol. 72, No. 3, 2002, pp. 486–487. Translated from Zhurnal Obshchei Khimii, Vol. 72, No. 3, 2002, pp. 521–522.
Original Russian Text Copyright © 2002 by Yarkevich, Tsvetkov.

LETTERS TO THE EDITOR

(Chloromethyl)phosphoryl Compounds in the Arbuzov Reaction

A. N. Yarkevich and E. N. Tsvetkov[†]

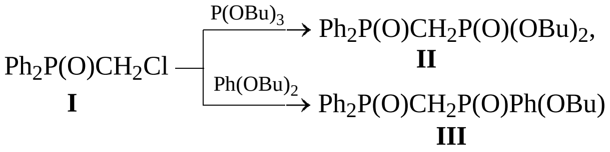
Institute of Physiologically Active Compounds, Russian Academy of Sciences, Chernogolovka, Russia

Received April 4, 2001

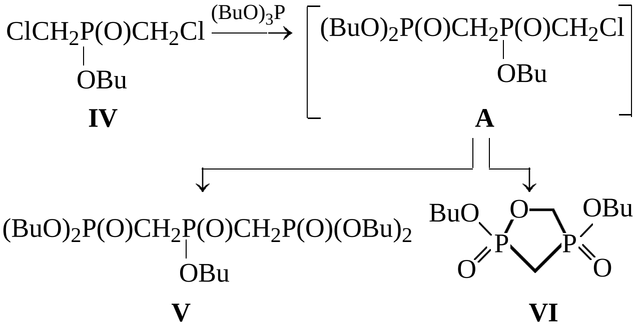
The synthesis of di- and triphosphoryl compounds containing the potent complex-forming methylenediphosphoryl fragments was carried out with the purpose of searching for effective extractants and selective complex-forming agents.

(Chloromethyl)diphenylphosphine oxide (**I**) was used as the haloalkyl component in the Arbuzov reaction for preparing unsymmetrical diphosphoryl compounds containing a phosphine oxide group. It was previously shown [1, 2] that the reactivity of compound **I** is relatively low, and we took this into account when choosing reaction conditions.

By reacting phosphine oxide **I** with tributyl phosphite and dibutyl phenylphosphonite at 190–210°C, respectively, we synthesized dibutyl (diphenylphosphorylmethyl)phosphonate (**II**) and butyl (diphenylphosphorylmethyl)phenylphosphinate (**III**).



Butyl bis(chloromethyl)phosphinate (**IV**) was chosen as the haloalkyl component for preparing triphosphoryl compounds. The reaction of phosphinate **IV** with tributyl phosphite in a 1:2 molar ratio gives pentabutyl ester **V**, a traditional Arbuzov product. At an equimolar ratio of the starting compounds, cyclic diphospholane **VI** was obtained instead of the expected butyl (chloromethyl)(dibutoxyphosphorylmethyl)phosphinate (**A**), according to the above-presented scheme.



(Chloromethyl)phosphonophosphinate **A** formed in the first stage is likely to react with tributyl phosphite to give ester **V**, while in the absence of tributyl phosphite it undergoes intramolecular cyclization leading to diphospholane **VI**. In this case, the high temperature of the process and removal of butyl chloride from the reaction sphere favor cyclization. Similar formation of stable five-membered rings, (1,2-oxaphospholanes) was previously observed on attempted preparation of (3-halopropyl)phosphonates [3, 4] and also while using them as alkylating agents in polar media [4].

The reaction was carried out in a Claisen flask equipped with a dropping funnel for adding tributyl phosphite and a condenser with a receiver for collecting condensate. For a more complete removal of the evolving butyl chloride and prevention of its participation in the Arbuzov reaction, reduced pressure (180 mm) was maintained in the reaction vessel. The reaction completion was detected by the amount of the condensate. The reaction progress was also controlled by ^{31}P NMR spectroscopy.

The starting chloromethyl compounds **I** and **II** were prepared by known procedures [5, 6]. Tributyl phosphite and dibutyl phenylphosphonite were distilled in a vacuum before use.

Dibutyl (diphenylphosphorylmethyl)phosphonate (II). Tributyl phosphite, 7.28 g, was added for 5 h at 190–200°C (bath temperature) and a residual pressure of 180 mm to a melt of 5.13 g of $Ph_2P(O)\cdot CH_2Cl$ (**I**). The resulting mixture was kept for 2 h at

---

[†] Deceased.

1070-3632/02/7203-0486 $27.00 © 2002 MAIK "Nauka/Interperiodica"

the same temperature. The volatile fraction containing, according to the ^{31}P NMR spectra, mainly $(BuO)_3P$, $(BuO)_3PO$, and $(BuO)_2P(O)Bu$ was removed in a water-jet-pump vacuum at 130–140°C (10 mm). The residual oil was chromatographed on a column of Silica gel L (100–160 μm), eluent hexane–isopropanol, 7 : 1, to obtain 0.609 g (75%) of phosphonate **II**, mp 53–54°C. ^{1}H NMR spectrum, δ, ppm: 0.96 t (6H, 2Me), 1.24 m (4H, 2CH$_2$CCO0, 1.46 m (4H, 2CH$_2$CO), 3.00 m (2H, PCH$_2$P), 3.96 m (4H, 2CH$_2$O), 7.44 m (6H) and 7.82 m (4H) (2Ph). ^{31}P NMR spectrum, δ_P, ppm : 20.22 d and 24.80 d (J_{PP} 14.6 Hz). Found, %: C 61.62, 61.60; H 7.29, 7.22; P 14.61, 14.56. $C_{21}H_{30}O_4P_2$. Calculated, %: C 61.76; H 7.40; P 15.71.

Butyl (diphenylphosphorylmethyl)phenylphosphinate (III). *a*. The synthesis was performed by a procedure similar to that applied for phosphonate **II**, by heating 6.27 g of $Ph_2P(O)CH_2Cl$ and 9.33 g of $PhP(OBu)_2$ at 200–210°C. The oily reaction product (7.20 g, 70%) was crystallized by treatment with ether. Crystallization from isoamyl acetate gave 6.00 g (58%) of phosphinate **III**, mp 99.5–100.5°C. ^{1}H NMR spectrum, δ, ppm: 0.86 t (3H, Me), 1.16 m (2H, CH$_2$CCO), 1.38 m (2H, CH$_2$CO), 3.16 m (2H, PCH$_2$P), 3.76 m (2H, CH$_2$O), 7.40 m (9H) and 7.82 m (6H) (3Ph). ^{31}P NMR spectrum, δ, ppm: 24.48 d and 34.38 d (J_{PP} 12.6 Hz). Found, %: C 66.84, 66.91; H 5.97, 6.01; P 15.25, 15.47. $C_{23}H_{26}O_3P_2$. Calculated, %: C 66.98; H 6.36; P 15.02.

b. A mixture of 7.50 g of $Ph_2P(O)CH_2Cl$ and 11.22 g of $PhP(OBu)_2$ was heated for 8 h at 200–210°C (bath temperature) in a water-jet-pump vacuum (20–30 mm). The reaction mixture was cooled, and the resulting oil was crystallized by treatment with ether to obtain 10.50 g (85%) of phosphinate **III**, mp 97–99°C.

Butyl bis(dibutoxyphosphorylmethyl)phosphinate (V) was prepared similarly to phosphonate **II** from 5.48 g of phosphinate **IV** and 18.77 g of tributyl phosphite. Yield 12.23 g (92%), oil. ^{1}H NMR spectrum, δ, ppm: 0.92 t (15H, 5 Me), 1.40 m (10 H, 5CH$_2$CCO), 1.66 m (10 H, 5CH$_2$CO), 2.80 m (4H, CH$_2$PCH$_2$), 4.10 m (10 H, 5CH$_2$O). ^{31}P NMR spectrum, δ_P, ppm: 20.19 d and 38.34 t (J_{PP} 3.2 Hz). Found, %: C 49.24, 49.18; H 8.81, 8.97; P 17.38, 17.32. $C_{22}H_{49}O_8P_3$. Calculated, %: C 49.43; H 9.24; P 17.38.

2,4-Dibutoxy-1,2,4-oxadiphospholane (VI) was prepared similarly to phosphonate **II** from 5.48 g of phosphinate **IV** and 6.26 g of tributyl phosphite. Yield 5.87 g (83%), bp 200–205°C (0.5 mm). ^{1}H NMR spectrum, δ, ppm: 0.94 t (6H, 2 Me), 1.44 m (4H, 2CH$_2$CCO), 1.72 m (4H, 2CH$_2$CO), 2.68 m (2H, PCH$_2$P), 3.84 m (2H, PCH$_2$OP), 4.18 m (4H, 2CH$_2$O). ^{31}P NMR spectrum, δ_P, ppm: 19.29 s and 39.24 s. Found, %: C 42.00, 41.86; H 8.10, 8.04; P 17.38, 17.32. $C_{10}H_{22}O_5P$. Calculated, %: C 42.25; H 7.80, P 21.80.

The ^{1}H and ^{31}P NMR spectra were registered on a Bruker CXP spectrometer at 200 (^{1}H) and 81 MHz (^{31}P) in $CDCl_3$ against internal TMS and external 85% phosphoric acid. The melting points were measured on a Boetius PHMK 05 device.

ACKNOWLEDGMENTS

The authors express their gratitude to V.O. Zavel’skii for measuring the NMR spectra and to V.V. Ragulin for discussing the resulting data.

REFERENCES

1. Hellmann, H. and Bader, J., *Tetrahedron Lett.*, 1961, no. 20, pp. 724–729.
2. Kreutzkamp, N, Herberg, K., Lammerhirt, K., and Schmidt-Samoa, E., *Arch. Pharm.*, 1971, vol. 304, no. 12, pp. 896–899.
3. Pudovik, A.N., Muratova, A.A., and Savel’eva, V.A., *Zh. Obshch. Khim.*, 1964, vol. 34, no. 8, pp. 2582–2586.
4. Rozhko, L.F., Ragulim, V.V., and Tsvetkov, E.N., *Zh. Obshch. Khim.*, 1996, vol. 66, no. 7, pp. 1093–1095.
5. Patsanovskii, I.I., Ishmaeva, E.A., Sundukova, E.N., Yarkevich, A.N., and Tsvetkov, E.N., *Zh. Obshch. Khim.*, 1986, vol. 56, no. 3, pp. 567–576.
6. Maier, L., *Helv. Chim. Acta*, 1969, vol. 52, p. 827.