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SHORT COMMUNICATIONS

Dedicated to the 100th Anniversary of Corresponding Member of the Russian Academy of Sciences A.A. Petrov

Synthesis and Structure of Aminomethylphosphabetaines

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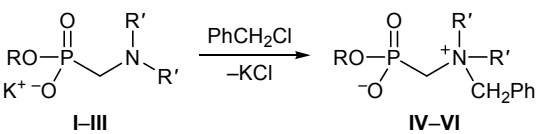
It is known that some dialkyl aminoalkylphosphonates in solution spontaneously undergo intramolecular O→N migration of alkyl group with formation of zwitterionic alkyl ammonioalkylphosphonates which may be regarded as synthetic analogs of phosphono- and phospholipids capable of acting as mono- and multidentate ligands in donor–acceptor complexes with some Lewis acids [1]. While searching for efficient and selective liquid and membrane extractants for various substrates, we have developed a new convenient procedure for the synthesis of phosphabetaines. This procedure implies *N*-alkylation of potassium alkyl aminomethylphosphonates prepared by hydrolysis of the corresponding dialkyl aminomethylphosphonates with aqueous sodium hydroxide. Alkyl hydrogen aminomethylphosphonates (RO)(OH)P(O)$CH_2NR'R'$ were synthesized in almost quantitative yield (according to the ^{31}P NMR data) by the Kabachnik–Fields reaction [2] and were converted without isolation and special purification into potassium salts **I**–**III**. The latter were purified by treatment with ethyl acetate; nonpolar organic impurities were thus removed, whereas salts **I**–**III** did not dissolve. If this procedure was inefficient, the salts were dissolved in methanol, and small amount of dilute hydrochloric acid was added to the solution. Solid impurities were filtered off, and the alkyl hydrogen phosphonate was converted again into potassium salt by adding an equimolar amount of 50% aqueous potassium hydroxide.



I–**III** **IV**–**VI**

I, **IV**, R = Et, R′ = Pr; **II**, **V**, R = R′ = Bu; **III**, **VI**, R = *iso*-C_5H_{11}, R′ = Bu.

Quaternization of potassium salts with benzyl chloride gave zwitterionic ammoniomethylphosphonates **IV**–**VI** as well shaped crystals, which can be readily purified by recrystallization from methanol or ethyl acetate.

The structure of **IV**–**VI** was determined on the basis of their IR and ^1H and ^{31}P NMR spectra, and the structure of ethyl [benzyl(dipropyl)ammoniomethyl]-phosphonate (**IV**) was proved by the X-ray diffraction data. More detailed information on the structure and properties of new phosphabetaines will be reported elsewhere. The synthesis of dialkyl aminomethylphosphonates was described in [2].

Potassium ethyl [(dipropylamino)methyl]phosphonate (I). Yield 75%, mp 188°C. IR spectrum (mineral oil), ν, cm^{-1}: 1104 (P=O), 1061 (P–O–C). ^1H NMR spectrum ($CDCl_3$, 300 MHz), δ, ppm: 0.86 t (3H, C**H**$_3$CH$_2$, $^3J_{HH}$ = 7.28 Hz), 1.23 t (6H, CH_3, $^3J_{HH}$ = 7.04 Hz), 1.39–1.52 m (4H, NCH_2C**H**$_2$), 2.52–2.65 d.d (2H, PCH_2) and t (4H, NCH_2); 3.86–3.95 m (OCH_2). ^{31}P NMR spectrum (dioxane, 122.4 MHz): δ_P 20.4 ppm.

Potassium butyl [(dibutylamino)methyl]phosphonate (II). Yield 78%, mp 205°C. IR spectrum (mineral oil), ν, cm^{-1}: 1194 (P=O), 1061 (P–O–C). ^1H NMR spectrum ($CDCl_3$, 300 MHz), δ, ppm: 0.95 t (9H, CH_3, $^3J_{HH}$ = 7.24 Hz), 1.23–1.67 m (12H, CH_2), 2.57–2.74 t (NCH_2), 2.69 d (2H, PCH_2, $^2J_{PH}$ = 12.80 Hz), 3.81–3.91 m (2H, OCH_2). ^{31}P NMR spectrum (dioxane, 122.4 MHz): δ_P 21.3 ppm.

Potassium 3-methylbutyl [(dibutylamino)methyl]phosphonate (III). Yield 80%, mp 198°C. IR spec-

trum (mineral oil), ν, cm^{-1}: 1201 (P=O), 1064 (P–O–C). ^1H NMR spectrum ($CDCl_3$, 300 MHz), δ, ppm: 0.85–0.93 m (12H, CH_3), 1.19–1.72 m (11H, CH_2, CH), 2.50–2.66 d (2H, PCH_2) and t (4H, NCH_2), 3.53–3.87 m (2H, OCH_2). ^{31}P NMR spectrum (dioxane, 122.4 MHz): δ_P 19.8 ppm.

Ethyl [benzyl(dipropyl)ammoniomethyl]phosphonate (IV). Yield 87%, mp 132.5°C. IR spectrum (mineral oil), ν, cm^{-1}: 1466–1460 (Ph), 1081 (P=O), 1054 (P–O–C). ^1H NMR spectrum ($CDCl_3$, 300 MHz), δ, ppm: 0.97 t (3H, CH_3, $^3J_{HH}$ = 7.24 Hz), 1.22 t (6H, CH_3, $^3J_{HH}$ = 7.05 Hz), 1.72–1.93 m (4H, $NCH_2C\mathbf{H}_2$), 3.13 d (2H, PCH_2, $^2J_{PH}$ = 12.15 Hz), 3.04–3.15 d.t and 3.24–3.36 d.t (2H each, NCH_2, $^2J_{HH}$ = 4.8, $^3J_{HH}$ = 12.6 Hz), 3.95–4.05 m (OCH_2, $^3J_{HH}$ = 7.16 Hz), 4.84 s ($C\mathbf{H}_2Ph$), 7.40–7.44 m (3H, *m*-H, *p*-H), 7.57–7.61 (2H, *o*-H). ^{31}P NMR spectrum ($CHCl_3$, 122.4 MHz): δ_P 4.3 ppm.

Butyl [benzyl(dibutyl)ammoniomethyl]phosphonate (V). Yield 84%, mp 110.3°C. IR spectrum (mineral oil), ν, cm^{-1}: 1466–1458 (Ph), 1081 (P=O). ^1H NMR spectrum ($CDCl_3$, 300 MHz), δ, ppm: 0.93 t (6H, CH_3, $^3J_{HH}$ = 7.36 Hz), 1.04 t (3H, CH_3, $^3J_{HH}$ = 7.30 Hz), 1.21–1.95 m (12H, CH_2), 3.21 d (2H, PCH_2, $^2J_{PH}$ = 12.09 Hz), 3.17–3.28 d.t and 3.37–3.48 d.t (2H each, NCH_2), 3.97–4.05 m (OCH_2), 4.94 s ($C\mathbf{H}_2Ph$), 7.46–7.54 (3H, *m*-H, *p*-H), 7.66–7.72 (2H, *o*-H). ^{31}P NMR spectrum ($CHCl_3$, 122.4 MHz): δ_P 4.2 ppm.

3-Methylbutyl [benzyl(dibutyl)ammoniomethyl]-phosphonate (VI). Yield 89%, mp 107.5°C. IR spectrum (mineral oil), ν, cm^{-1}: 1462–1468 (Ph), 1083 (P=O). ^1H NMR spectrum ($CDCl_3$, 300 MHz), δ, ppm: 0.76–0.84 t (6H, CH_3), 0.91 t (6H, CH_3, $^3J_{HH}$ = 7.31 Hz), 1.05–1.83 m (11H, CH_2, CH), 3.07 d (2H, PCH_2, $^2J_{PH}$ = 12.10 Hz), 3.05–3.19 d.t and 3.23–3.34 d.t (2H each, NCH_2), 3.86–3.96 m (OCH_2), 4.81 s ($C\mathbf{H}_2Ph$), 7.32–7.41 (3H, *m*-H, *p*-H), 7.54–7.58 (2H, *o*-H). ^{31}P NMR spectrum ($CHCl_3$, 122.4 MHz): δ_P 4.2 ppm.

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