

Reaction of Diethyl Vinylphosphonate with Octyl- and Dodecylamines

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Abstract—Diethyl vinylphosphonate reacted with octyl- and dodecylamines to give the corresponding addition products which underwent dealkylation via elimination of ethylene molecule with formation of crystalline zwitterionic ethyl 2-(alkylammonio)ethylphosphonates.

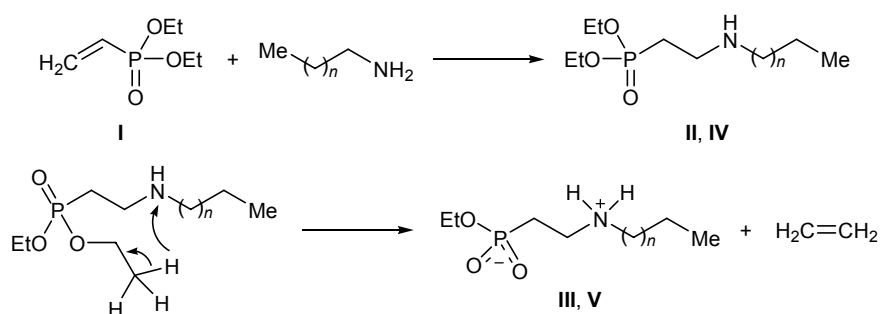
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Four-coordinate phosphorus derivatives comprising a phosphorus–carbon bond and a nitrogen-containing fragment are promising as biologically active substances, extractants, and membrane carriers [1–3]. The most rational method of synthesis of phosphorylated alkanes functionalized with a β -aminoalkyl group is based on the addition of primary and secondary amines to the double bond of alkenylphosphonates [4]. Introduction of long-chain aminoalkyl fragments into phosphonate molecules leads to compounds with improved membrane transport properties and enhanced biological activity.

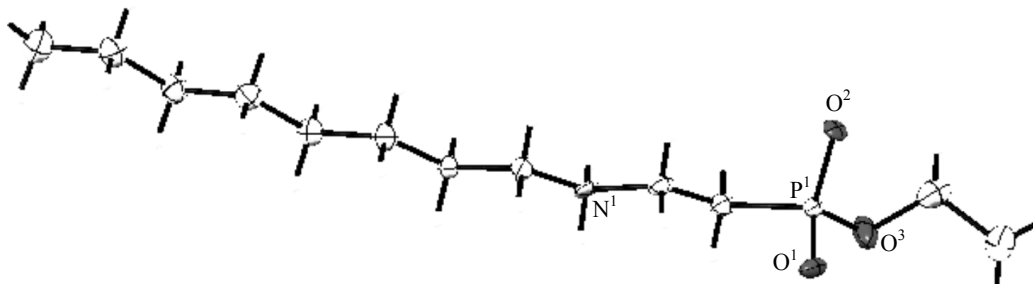
With a view to obtain such derivatives, we examined the reaction of diethyl vinylphosphonate (**I**) with octyl- and dodecylamines. Phosphonate **I** reacted with an equimolar amount of octylamine to give a thick oily

material (compound **II**) which was washed with petroleum ether until constant refractive index. The IR spectrum of **II** displayed no absorption band at 1640 cm^{-1} assignable to C=C stretching vibrations, while N–H and P=O stretching vibrations bands were present at 3200 and 1240 cm^{-1} , respectively. The ^{31}P NMR spectrum of **II** contained only one signal at δ_{P} 30.5 ppm. The presence in the ^1H NMR spectrum of **II** of a doublet of triplets at δ 1.7 ppm ($^2J_{\text{PH}} = 18.3$, $^3J_{\text{HH}} = 7.2$ Hz) due to protons in the methylene group attached to phosphorus indicated addition of octylamine to the β -carbon atom of the vinyl group. Taking into account the above spectral characteristics and elemental composition, the addition product was assigned the structure of diethyl 2-(octylamino)ethylphosphonate (**II**). Phosphonate **II** on storage underwent transformation

Scheme 1.



II, III, $n = 6$; **IV, V**, $n = 10$.



Structure of the molecule of ethyl 2-(octylammonio)ethylphosphonate (**III**) in crystal according to the X-ray diffraction data.

into crystalline compound **III** which was poorly soluble in organic solvents. The melting point of **III** (227°C) was measured by simultaneous thermogravimetry and differential scanning calorimetry (TG–DSC) using a micro thermal analyzer coupled with a quadrupole mass spectrometer. The molecular and crystal structures of compound **III** were determined by X-ray analysis (see figure).

The X-ray diffraction data will be reported in detail elsewhere. According to these data, compound **III** has the structure of ethyl 2-(octylammonio)ethylphosphonate. Such zwitterionic structures are formed as a result of easy elimination of ethylene molecule from the phosphoryl fragment. Inner salts were obtained previously in the reactions of vinylphosphonates with primary amines [5]; dealkylation of four-coordinate phosphorus acid esters with elimination of alkene was also reported [6].

Phosphonate **I** reacted with dodecylamine in a similar way to afford diethyl 2-(dodecylamino)ethylphosphonate (**IV**) whose subsequent dealkylation with elimination of ethylene produced crystalline zwitterionic compound **V** with mp 197°C.

Thus, products of long-chain alkylamine addition to diethyl vinylphosphonate readily undergo dealkylation via elimination of ethylene with formation of zwitterionic compounds.

EXPERIMENTAL

The IR spectra were recorded on a Specord M-80 spectrometer. The ^1H and ^{31}P NMR spectra were measured on a Varian Unity-300 instrument at 300 and 121.4 MHz, respectively. The chemical shifts were determined relative to the residual proton signal of the deuterated solvent (^1H) or 85% H_3PO_4 (^{31}P , external reference). The purity and thermal stability of compounds **III** and **V** were estimated by simultaneous thermogravimetry and differential scanning calorimetry (TG–DSC) using an STA 449C Jupiter micro

thermal analyzer coupled with a QMS 403C Aeolos quadrupole mass spectrometer (Netzsch, Germany).

Diethyl 2-(octylamino)ethylphosphonate (II). Octylamine, 1.29 g (0.1 mmol), was added to 1.7 g (0.1 mmol) of diethyl vinylphosphonate (**I**). After several days, the resulting thick oily material was repeatedly washed with petroleum ether until constant refractive index, $n_D^{20} = 1.4384$. Yield 1.87 g (63%). ^1H NMR spectrum (CDCl_3), δ , ppm: 0.59 t [3H, $\text{CH}_3(\text{CH}_2)_6$, $^3J_{\text{HH}} = 6.7$ Hz], 0.99 br.s [12H, $(\text{CH}_2)_6$], 1.05 t (6H, $\text{CH}_3\text{CH}_2\text{O}$, $^3J_{\text{HH}} = 7.1$ Hz), 1.57 br.s (NH), 1.70 d.t (2H, PCH_2 , $^2J_{\text{PH}} = 18.3$, $^3J_{\text{HH}} = 7.2$ Hz), 2.31 d.t (2H, NCH_2 , $^3J_{\text{HH}} = 7.2$, $^2J_{\text{HH}} = 6.8$ Hz), 2.61 d.d.d. (2H, $\text{PCH}_2\text{CH}_2\text{N}$, $^3J_{\text{PH}} = 15.1$, $^3J_{\text{HH}} = 7.2$, $^2J_{\text{HH}} = 6.8$ Hz), 3.80 m (2H, CH_2O). Found, %: C 56.9; H 10.7. $\text{C}_{14}\text{H}_{32}\text{NO}_3\text{P}$. Calculated, %: C 57.3; H 10.9.

Ethyl 2-(octylammonio)ethylphosphonate (III). After storage of compound **II** for 1.5 month, crystals insoluble in organic solvents separated, mp 227°C (decomp.). Found, %: C 54.8; H 10.8. $\text{C}_{12}\text{H}_{28}\text{NO}_3\text{P}$. Calculated, %: C 54.4; H 10.5.

Diethyl 2-(dodecylamino)ethylphosphonate (IV). A solution of 1.43 g (0.07 mmol) of dodecylamine in 2 mL of ethanol was added to 1.18 g (0.07 mmol) of phosphonate **I**. The solvent was removed to leave a very thick tarry material which was washed with petroleum ether. Yield 1.36 g (52%). ^1H NMR spectrum (CDCl_3), δ , ppm: 0.89 t [3H, $\text{CH}_3(\text{CH}_2)_{10}$, $^3J_{\text{HH}} = 6.5$ Hz], 1.19 br.s [20H, $(\text{CH}_2)_{10}$], 1.25 t (6H, $\text{CH}_3\text{CH}_2\text{O}$, $^3J_{\text{HH}} = 7.1$ Hz), 2.27 m (2H, PCH_2 , $^2J_{\text{PH}} = 18.6$ Hz), 2.86 t (2H, NCH_2 , $^3J_{\text{HH}} = 7.7$ Hz), 3.16 m (2H, $\text{PCH}_2\text{CH}_2\text{N}$), 4.05 m (2H, CH_2O). ^{31}P NMR spectrum (CDCl_3): $\delta_{\text{p}} 28$ ppm. Found, %: C 62.2; H 11.2. $\text{C}_{18}\text{H}_{40}\text{NO}_3\text{P}$. Calculated, %: C 61.9; H 11.5.

Ethyl 2-(dodecylammonio)ethylphosphonate (V). After storage of compound **IV** for several days, crystals insoluble in organic solvents separated, mp 197°C. Found, %: C 61.4; H 11.5. $\text{C}_{16}\text{H}_{36}\text{NO}_3\text{P}$. Calculated, %: C 61.8; H 11.6.

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