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LETTERS TO THE EDITOR

Synthesis of β-Enaminophosphonates and β-Methoxyiminophosphonates

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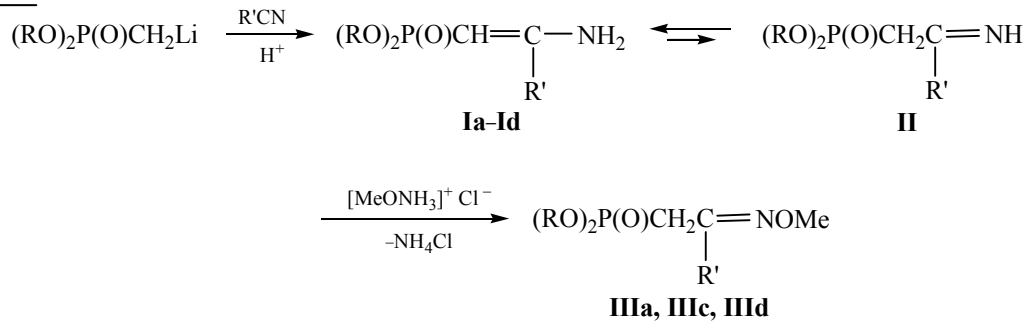
We found that reaction of dialkyl lithiummethylphosphonate with nitriles in THF proceeds at low temperature resulting in β-enaminophosphonates **Ia–Id** in high yields. They are stable liquids, which are easily distilled in a vacuum. β-Enaminephosphonates **I** are prototropic forms of iminophosphonates **II**. However, the tautomeric equilibrium **I** $\rightleftarrows$ **II** is shifted to enamine form **I**, what is unambiguously indicated by the NMR spectra. They content clear doublet signal of PCH-group proton and two protons of NH_2-group. At the same time β-enaminophosphonates enter easily into the reaction with methyl ether of hydroxylamine typical of imine compound, to form the previously unknown β-methoxyiminophosphonates **III** in quantitative yields [1, 2]. The ^1H and ^{31}P NMR spectra of compounds **III** confirm their structure: δ_P values are shifted to 30 ppm, and in the ^1HMR spectra there is a doublet signal belonging to the two protons of PCH_2-group.



R = Me, R' = Ph (**a**), R = Et, R' = C_6H_4F (**b**), R = Et, R' = Furyl (**c**), R = Et, R' = CF_3 (**d**).

Dimethyl [(*E*)-2-amino-2-phenylethenyl] phosphonate (Ia). To a solution of dimethyl lithiummethylphosphonate generated from 0.01 mol of dimethyl methylphosphonate and 0.011 mol of butyllithium in 5 ml of THF at –80ºC was added a solution of 0.01 mol of benzonitrile in 3 ml of THF. The reaction mixture was stirred for 3 h at this temperature. Then the temperature was increased to +20°C, and 10 ml of the saturated aqueous solution of NH_4Cl was added. The organic layer was separated. The water layer was extracted with ethyl acetate. This extract was dried with anhydrous Na_2SO_4 and concentrated in a vacuum. Yield 75%, bp 142°C (0.045 mm Hg), R_f 0.45 (Silufol, ethyl acetate). ^1H NMR spectrum ($CDCl_3$), δ_H, ppm: 1.32 t (6H, *J* 6.9, CH_3), 4.1 d (1H, PCH, *J* 12 Hz), 4.05 m (4H, OCH_2), 5.9 br (2H, NH_2), 7.38–7.54 m (C_6H_5). ^{31}P NMR spectrum ($CDCl_3$), δ_P, ppm: 28.8. Found, %: N 6.20; P 13.65. $C_{10}H_{14}NO_3P$. Calculated, %: N 6.17; P 13.63.

Diethyl [(*E*)-2-amino-2-(4-fluorophenyl)ethenyl] phosphonate (Ib) was prepared similarly. Yield 48%,

bp 165°C (0.03 mm Hg). ^{1}H NMR spectrum ($CDCl_3$), δ_H, ppm: 1.33 t (6H, CH_3, *J* 7.2 Hz), 4.06 m (4H, OCH_2), 4.08 d (1H, PCH=, *J* 10.2 Hz), 5.86 br (2H, NH_2), 7.07 and 7.56 m (4H, C_6H_4). ^{31}P NMR spectrum ($CDCl_3$), δ_P, ppm: 25.9. ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: –106.2. Found, %: N 5.18; P 11.32. $C_{12}H_{17}FNO_3P$. Calculated, %: N 5.13; P 11.34.

Diethyl [(*E*)-2-amino-2-(2-furanyl)ethenyl]phosphonate (Ic) was prepared similarly. Yield 74%, bp 152–155°C (0.03 mm Hg), R_f 0.43 (Silufol, ethyl acetate). ^{1}H NMR spectrum ($CDCl_3$), δ_H, ppm: 1.33 t (6H, CH_3, *J* 6.9 Hz), 4.06 m (4H, OCH_2), 4.46 d (1H, PCH, *J* 10.8 Hz), 5.98 br (2H, NH_2), 6.47 d (1H, *J* 3.5 Hz), 6.73 d (1H, *J* 3.5 Hz), 7.46 s (1H, furyl). ^{31}P NMR spectrum ($CDCl_3$), δ_P, ppm: 26.6. Found, %: N 5.74; P 12.60. $C_{10}H_{16}NO_4P$. Calculated, %: N 5.71; P 12.63.

Diethyl [(1*E*)-2-amino-3,3,3-trifluoro-1-propenyl]phosphonate (Id) was prepared similarly. Yield 50%, bp 118°C (0.04 mm Hg). ^{1}H NMR spectrum ($CDCl_3$), δ_H, ppm: 1.3 t (6H, CH_3, *J* 6.6 Hz), 3.1 d (1H, PCH, *J* 24 Hz), 4.06 m (4H, OCH_2), 6.14 br (2H, NH_2). ^{31}P NMR spectrum ($CDCl_3$), δ_P, ppm: 30.64. ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: 106.2. Found, %: F 23.36; N 5.61; P 12.6. $C_7H_{13}F_3NO_3P$. Calculated, %: F 23.06; N 5.67; P 12.5.

Dimethyl [(2*E*)-2-(methoxyimino)-2-phenylethyl]phosphonate (IIIa). To a solution of 1.33 g (5 mmol) of enamine **Ia** in 3 ml of anhydrous methanol was added a solution of 0.46 g (5.5 mmol) of $MeONH_2 \cdot HCl$ in 3 ml of anhydrous methanol at room temperature. Then the reaction mixture was heated for 3–5 min at 80°C. The solvent was evaporated and the residue was dissolved in ethyl acetate, filtered, concentrated, and distilled in a vacuum. Yield 75%, bp 140°C (0.05 mm Hg). ^{1}H NMR spectrum ($CDCl_3$), δ_H, ppm: 3.46 d (2H, PCH_2, *J* 23.7 Hz), 3.67 d (6H, CH_3O, *J* 11.5 Hz), 4.04 s (3H, CH_3O), 7.37 m, 7.71 m (5H, C_6H_5). ^{31}P ($CDCl_3$), δ_P, ppm: 30. Found, %: N 5.40; P 12.05. $C_{11}H_{16}NO_4P$. Calculated, %: N 5.45; P 12.04.

Diethyl [(2*E*)-2-(2-furanyl)-2-(methoxyimine)ethyl]phosphonate (IIIc) was prepared similarly. Yield 79%, bp 132–135°C (0.045 mm Hg). ^{1}H NMR spectrum ($CDCl_3$), δ_H, ppm: 1.25 t (6H, CH_3, *J* 6.6 Hz), 3.35 d (1H, PCH_2, *J* 23.1 Hz), 4.02 s (CH_3O), 4.06 m (4H, OCH_2), 6.45 d. d (1H, *J* 1.5, *J* 3 Hz), 6.75 d (1H, *J* 3.5 Hz), 7.46 s (1H). ^{31}P NMR spectrum ($CDCl_3$), δ_P, ppm: 30. Found, %: N 6.01; P 11.26. $C_{11}H_{18}NO_5P$. Calculated, %: N 5.09; P 11.25.

Diethyl [(2*E*)-3,3,3-trifluoro-2-(methoxyimino)propyl]phosphonate (IIId) was prepared similarly. Yield 82%, bp 118–120°C (0.04 mm Hg). ^{1}H NMR spectrum ($CDCl_3$), δ_H, ppm: 1.32 t (6H, CH_3, *J* 7 Hz), 3.1 d (2H, PCH_2, *J* 24 Hz), 4.04 s (3H, OCH_3), 4.09 m (4H, OCH_2). ^{31}P NMR spectrum ($CDCl_3$), δ_P, ppm: 30. Found, %: N 5.16; P 11.19. $C_8H_{15}F_3NO_4P$. Calculated, %: N 5.05; P 11.17.

The NMR spectra were registered on a Varian-300 spectrometer relative to internal TMS (^{1}H and ^{13}C) and 85% H_3PO_4 in D_2O (^{31}P). This work was supported by the grant STCU no. 3558.

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