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LETTERS TO THE EDITOR

Reaction of Aminoethynylphosphonates with Malononitrile

N. I. Svintsitskaya, A. V. Aleksandrova, A. V. Dogadina, and B. I. Ionin

St. Petersburg State Institute of Technology,
Moskovskii pr. 26, St.Petersburg, 190013 Russia
e-mail: ana_alexandrova@mail.ru; bi@thesa.ru

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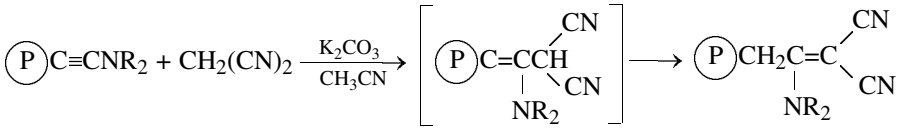
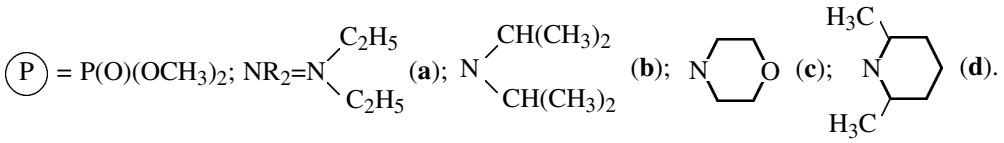
Acetylenes with acceptor groups are known to be highly active in the Michael addition reaction of compounds with active methylene group. This property has been widely used as a route to formation of a new carbon–carbon bond [1]. Thus, the reaction of (ethyne-1,2-diyl)diphosphonates with malononitrile in the presence of equimolar amount of potassium carbonate in anhydrous acetonitrile afforded 2-cyano-2-potassio-3,4-bis(dialkoxyphosphinoyl)but-3-enoates whose protonation gave corresponding CH derivatives [2].

We found that aminoethynylphosphonates readily react with malononitrile in the presence of potassium carbonate. The reaction proceeds as nucleophilic addition at the triple bond to form (2-amino-3,3-dicyanoprop-2-enyl)phosphonates **Ia**–**Id**. The reactions were performed in absolute acetonitrile by heating equimolar quantities of aminoethynylphosphonate and CH acid for 1–1.5 h. A catalytic quantity of potassium carbonate (~5 mol%) was found enough for the reaction to occur.



Ia–Id



The reaction progress was monitored by means of ^{1}H, ^{13}C, ^{31}P NMR, and two-dimensional ^{1}H–{^{31}P} NMR spectroscopy. As the reaction occurred, a signal of methylene protons of the resulting adduct appeared and grew in the ^{1}H NMR spectrum (δ 3.16 ppm, ‘doublet, $^2J_{HP}$ 21.6 Hz). In the ^{31}P NMR spectra of the reaction mixtures, the signal with δ_P ~0 ppm (starting aminoethynylphosphonate) attenuated and disappeared completely; simultaneously, a signal of the product appeared downfield (δ_P 21.0 ppm) and grew.

In the ^{13}C NMR spectra of the reaction mixtures we observed appearance of a doublet signal of the carbon atom directly connected to phosphorus at δ_C 31.25 ppm with a large $^1J_{CP}$ coupling constant (137 Hz) and signals of the carbon atoms at the double bond shifted downfield to δ_C 160–163 ppm (doublet, $^2J_{CP}$ 5.9 Hz) and 56–57 ppm. Furthermore, there were two signals of nonequivalent CN groups at δ_C 116 and 117 ppm.

After the reaction had been complete, acetonitrile

was removed in a water-jet-pump vacuum. The yield of the crude product achieved 80%. Pure individual products were isolated by liquid chromatography on MN Kieselgel (60/0.025–0.004 mm), eluents carbon tetrachloride–acetone, 2 : 1 (**Ia**, **Ib**), and methylene chloride–acetone, 2 : 1 (**Ic**). Purified products were isolated in 30% yield. Compounds **Ia**–**Ic** are colored very viscous liquids which crystallized with time to give badly formed crystals. Compound **Id** precipitated from the reaction mixture as colorless plate crystals which were filtered off and purified additionally by recrystallization from benzene.

The starting aminoethynylphosphonates were prepared from dimethyl chloroethynylphosphonate and corresponding secondary amines [3]. All syntheses were carried out in carefully dried chemical glassware with dry reagents and absolute solvents to avoid formation of undesirable phosphorylated acetamides.

Dimethyl [3,3-dicyano-2-(diethylamino)prop-2-enyl]phosphonate (Ia). Light brown amorphous crystals. ^{1}H NMR spectrum, δ, ppm ($CDCl_3$): 1.21 t (6H, C*H*$_3$CH$_2$N), 3.10 d (2H, $^2J_{HP}$ 21.6 Hz, CH$_2$P), 3.63 br.q (4H, CH$_2$N), 3.75 d (6H, $^3J_{HP}$ 12.0 Hz, CH$_3$O). ^{13}C NMR spectrum, δ_C, ppm ($CDCl_3$): 13.06 (*C*H$_3$CH$_2$N), 31.12 d (CH$_2$P, $^1J_{PC}$ 136.4 Hz), 47.02 (CH$_3$*C*H$_2$N), 50.53 [*C*(CN)$_2$], 53.20 d (CH$_3$OP, $^2J_{CP}$ 5.8 Hz), 116.34, 117,87 (CN), 160.19 d [*C*=C(CN)$_2$, $^2J_{CP}$ 5.9 Hz]. ^{31}P NMR, δ_P, ppm ($CDCl_3$): 20.52.

Dimethyl [3,3-dicyano-2-(diisopropylamino)-prop-2-enyl]phosphonate (Ib). Red amorphous crystals. ^{1}H NMR spectrum, δ, ppm ($CDCl_3$): 1.36 t (6H, C*H*$_3$CH$_2$N), 3.26 d (2H, $^2J_{HP}$ 22.0 Hz, CH$_2$P), 3.72 q (4H, CH$_2$N), 3.79 d (6H, $^3J_{HP}$ 11.2 Hz, CH$_3$O). ^{13}C NMR spectrum, δ_C, ppm ($CDCl_3$): 22.28 (*C*H$_3$CH$_2$N), 33.19 d (CH$_2$P, $^1J_{PC}$ 132.8 Hz), 57.79 [*C*H(CH$_3$)$_2$], 53.22 d (CH$_3$OP, $^2J_{CP}$ 5.4 Hz), 56.03 [*C*(CN)$_2$], 116.03, 117.47 (CN), 163.76 d (=CN, $^2J_{CP}$ 7.1 Hz). ^{31}P NMR spectrum, δ_P, ppm ($CDCl_3$): 21.94.

Dimethyl [3,3-dicyano-2-(morpholin-4-yl)prop-2-enyl]phosphonate (Ic). Yellow amorphous crystals. ^{1}H NMR spectrum, δ, ppm ($CDCl_3$): 3.16 d (2H, $^2J_{HP}$ 21.0 Hz, CH$_2$P), 3.74 m [4H, (CH$_2$)$_2$N and 4H, (CH$_2$)$_2$O], 3.76 d (6H, $^3J_{HP}$ 10.8 Hz, CH$_3$O). ^{13}C NMR spectrum, δ_C, ppm ($CDCl_3$): 31.25 d (CH$_2$P, $^1J_{PC}$ 137.2 Hz), 50.99 [(CH$_2$)$_2$N], 53.43 d (CH$_3$OP, $^2J_{CP}$ 6.8 Hz), 57.60 [C(CN)$_2$], 65.98 [(CH$_2$)$_2$O], 115.59, 116.77 (CN), 162.70 d [C=C(CN)$_2$, $^2J_{CP}$ 5.8 Hz]. ^{31}P NMR spectrum, δ_P, ppm ($CDCl_3$): 21.16.

Dimethyl [3,3-dicyano-2-(2,6-dimethylpiperidin-1-yl)prop-2-enyl]phosphonate (Id). Colorless plates. ^{1}H NMR spectrum, δ, ppm ($CDCl_3$): 1.36 d (6H, J_{HH} 7.6 Hz, CH$_3$), 1.43–1.87 m (6H, β,β',γ-CH$_2$, piper.), 3.31 d (2H, $^2J_{HP}$ 21.8 Hz, CH$_2$P), 4.47–4.77 m (2H, α,α'-CH, piper.), 3.86 d (6H, $^3J_{HP}$ 10.4 Hz, CH$_3$O). ^{13}C NMR spectrum, δ_C, ppm ($CDCl_3$): 12.54 (CH$_3$), 21.53 (γ-CH$_2$, piper.), 29.95 (β-CH$_2$, piper.), 31.40 d (CH$_2$P, $^1J_{PC}$ 146.2 Hz), 32.55 (α-CH, piper.), 52.72 [*C*(CN)$_2$], 53.40 d (CH$_3$OP, $^2J_{CP}$ 5.6 Hz), 115.86, 118.23 (CN), 160.45 d [C=C(CN)$_2$, $^2J_{CP}$ 6.0 Hz]. ^{31}P NMR spectrum, δ_P, ppm ($CDCl_3$): 20.82.

Organic solvents and reagents were purified and dried by conventional procedures. The ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on Bruker C-400 (^{1}H) and Bruker C-200 (^{13}C and ^{31}P) spectrometers operated at 400, 50.328, and 81.014 MHz, respectively, in $CDCl_3$ against internal TMS (^{1}H, ^{13}C) and external 85% phosphoric acid (^{31}P). The routine ^{1}H and ^{1}H–{^{31}P} NMR spectra were recorded on a Tesla BS-497 instrument operated at 100/40 MHz.

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