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LETTERS TO THE EDITOR

To the 80th Anniversary of B.I. Ionin

Reaction of Chloroethynylphosphonates with 1-Methyl-3*H*-imidazole-2-thiones

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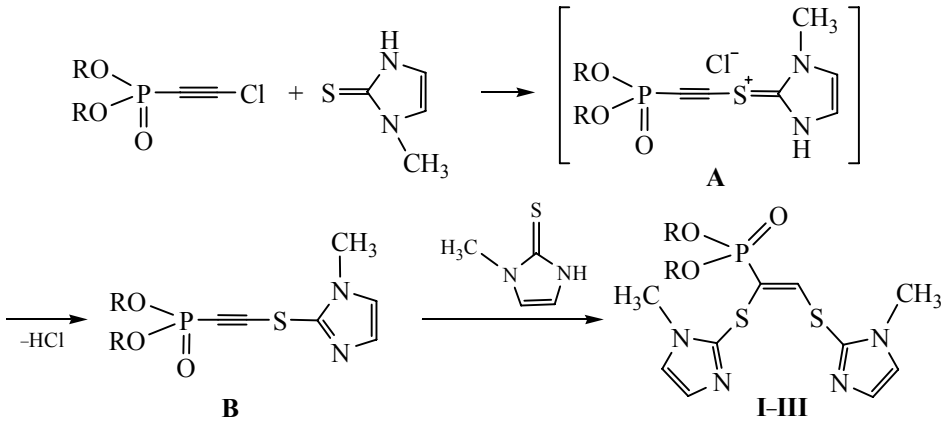
Recently we have found that reaction of chloroethynephosphonates with heterocyclic binucleophiles (triazole- and tetrazolethiones) involves the thione tautomer and yields heterobicyclic compounds [1, 2]. Reaction of the nucleophiles with chloroethynephosphonates in protic solvents (under conditions of the thiole form of the starting azolethiones prevailing) proceeds as substitution–addition affording linear alkenes [3]. Generation of minor linear compounds (up to 30%) has been observed in the reaction of chloroethynephosphonates with thione tautomer of tetrazoles, due to lability of hydrogen atom of the tetrazole ring [2–4].

In contrast, reaction of chloroethynephosphonates with 1-methyl-3*H*-imidazole-2-thione proceeded with high chemo- and regionselectivity resulting in preferential formation of the corresponding linear alkenephosphonates. At the same time, according to ^{15}N NMR spectroscopy, 1-methyl-3*H*-imidazole-2-thione existed in the thione tautomer form in aprotic solvents (DMSO or CH_3CN); that should have caused formation of the cyclic product in the considered reaction. However, performing the reaction with 1-methyl-3*H*-imidazole-2-thione in anhydrous acetonitrile at the reagents ratio of 1 : 2 upon vigorous stirring at room temperature gave dialkyl [*Z*-1,2-bis(1-methyl-1*H*-imidazol-2-ylsulfenyl)ethenyl]phosphonates **I**–**III** in yield of over 80% (Scheme 1).

The reaction most probably proceeded via the formation of sulfenium salt **A** which eliminated a molecule of hydrogen chloride due to presence of the

Scheme 1.



R = Me (**I**), Et (**II**), *i*-Pr (**III**).

labile proton in the imidazole ring, thus providing imidazolesulfenylethynephosphonate **B**. The latter further added the second molecule of thioimidazole to give ethenephosphonate **I**–**III**. Formation of the intermediate acetylene phosphonate **B** was detected by means of ^{31}P NMR spectroscopy (δ_P from –1 to –2 ppm).

Structures of phosphonates **I**–**III** were elucidated by ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy. Chemical shift of the phosphorus (δ_P 8–11 ppm) was within the range typical of the phosphonates with phosphorus–carbon (sp^2) bond. The olefin proton gave rise to a downfield-shifted doublet signal at 8.1–8.2 ppm with $^{3}J_{HP}$ 13.8 Hz (^{1}H NMR spectrum). The $^{3}J_{HP}$ value was in line with *Z*-configuration of alkenephosphonates **I**–**III** that was unambiguously confirmed by XRD. The protons at double bonds of the both imidazole rings of phosphonates **I** and **III** resonated as two weakly interacting AB-systems. The same protons were observed as three singlet signals in the ^{1}H NMR spectrum of phosphonate **II;** that could be explained by equivalence of the two chemical shifts and the absence of observable spin–spin coupling constants.

The thione structure of the starting thioimidazole was confirmed by analysis of the ^{15}N NMR spectra (the spectra were recorded in DMSO-d_6 without proton decoupling: a singlet at 161.19 ppm and a doublet at 166.39 ppm, $^{1}J_{HN}$ 99.5 Hz; as well as with proton decoupling: strong singlet at 162.62 ppm and a weaker singlet at 165.79 ppm). A singlet at 162.2 ppm and a quartet at 165.79 ppm with $^{2}J_{NH}$ 3.6 Hz were registered in the ^{15}N NMR spectrum of thioimidazole in CD_3OD without proton decoupling. The singlet nature of the signal of N^3 nitrogen atom could be explained by the exchange process. The values of the chemical shifts of the nitrogen atoms indicated the thione structure of the thioimidazole.

Dimethyl [*Z*-1,2-bis(1-methyl-1*H*-imidazol-2-yl-sulfenyl)ethenyl]phosphonate (I). A mixture of 0.0025 mol of chloroethynephosphonic acid dimethyl ester and 0.005 mol of 1-methyl-1,3*H*-imidazole-2-thione in 10 mL of anhydrous acetonitrile was stirred at room temperature during 6–10 h. The formed precipitate (0.54 g) of phosphonate **I** was filtered off. The solvent was removed, and the residue was recrystallized from ethanol. 0.3 g more of phosphonate **I** was isolated. Yield 93%, colorless crystals, mp 133–135°C (C_2H_5OH). ^{1}H NMR spectrum (CD_3OD, 400.13 MHz), δ, ppm: 3.76 d (6H, OCH_3, $^{3}J_{HH}$ 11.3 Hz), 4.07 s (3H, NCH_3), 7.81 d (1H, C<u>H</u>=CH, $^{3}J_{HH}$ 2.0 Hz), 7.86 d (1H, CH=C<u>H</u>, $^{3}J_{HH}$ 1.8 Hz), 7.91 d (1H, C<u>H</u>=CH, $^{3}J_{HH}$ 2.0 Hz), 7.92 d (1H, CH=C<u>H</u>, $^{3}J_{HH}$ 1.8 Hz), 8.21 d (2H, CH=, $^{3}J_{PH}$ 13.8 Hz). ^{13}C NMR spectrum (CD_3OD, 100.61 MHz), δ_C, ppm: 35.34 (NCH_3), 53.63 d (CH_3OP, $^{3}J_{PC}$ 6.1 Hz), 115.55 d (=CP, $^{1}J_{PC}$ 195.9 Hz), 121.72, 122.12 (CH_3N<u>C</u>H=), 126.39, 126.74 (=NCH=), 134.94 d (SCH=, $^{3}J_{PC}$ 4.0 Hz), 150.76, 150.96 (SC=N). ^{31}P NMR spectrum (CD_3OD, 161.98 MHz): δ_P 11.19 ppm. Mass spectrum: *m*/*z* 361.0567 $[M + H]^+$ (calculated for $C_{12}H_{17}N_4O_3PS_2$: *M* 360.3921).

Diethyl [*Z*-1,2-bis(1-methyl-1*H*-imidazol-2-yl-sulfenyl)ethenyl]phosphonate (II) was prepared similarly. Yield 86%, colorless crystals, mp 128–130°C (C_2H_5OH). ^{1}H NMR spectrum (CD_3OD, 400.13 MHz), δ, ppm: 1.29 t (6H, $OCH_2C\underline{H}_3$, $^{3}J_{HH}$ 7.0 Hz), 4.05 s (3H, NCH_3), 4.11 d. q (4H, $OC\underline{H}_2CH_3$, $^{3}J_{HH}$ 7.0, $^{3}J_{PH}$ 11.3 Hz), 7.80 s and 7.84 s (2H, C<u>H</u>=CH), 7.89 s (2H, CH=C<u>H</u>), 8.16 d (1H, =CH, $^{3}J_{PH}$ 13.8 Hz). ^{13}C NMR spectrum (CD_3OD, 100.61 MHz), δ_C, ppm: 15.16 d ($\underline{C}H_3CH_2$, $^{3}J_{PC}$ 6.1 Hz), 35.22 (CH_3N), 64.03 d ($CH_3\underline{C}H_2OP$, $^{3}J_{PC}$ 6.1 Hz), 116.70 d (=CP, $^{1}J_{PC}$ 195.2 Hz), 121.71, 122.21 ($CH_3N\underline{C}H$=), 126.53, 126.69 (=NCH=), 135.01 d (C=<u>C</u>H, $^{2}J_{PC}$ 7.4 Hz), 150.22, 150.44 (SC=N). ^{31}P NMR spectrum (CD_3OD, 161.98 MHz): δ_P 8.69 ppm. Mass spectrum: *m*/*z* 389.0872 $[M + H]^+$ (calculated for $C_{14}H_{21}N_4O_3PS_2$: *M* 388.4453).

Diisopropyl [*Z*-1,2-bis(1-methyl-1*H*-imidazol-2-yl-sulfenyl)ethenyl]phosphonate (III) was prepared similarly. Yield 79%, colorless crystals, mp 131–133°C (C_2H_5OH). ^{1}H NMR spectrum (CD_3OD, 400.13 MHz), δ, ppm: 1.27 d and 1.28 d [12H, $OCH(CH_3)_2$, $^{3}J_{HH}$ 6.2 Hz], 4.01 s (3H, NCH_3), 4.66 m [2H, $OC\underline{H}(CH_3)_2$, $^{3}J_{HH}$ 6.2, $^{3}J_{PH}$ 13.5 Hz], 7.35 d (1H, C<u>H</u>=CH, $^{3}J_{HH}$ 1.0 Hz), 7.58 d (1H, CH=C<u>H</u>, $^{3}J_{HH}$ 1.0 Hz), 7.67 d (1H, C<u>H</u>=CH, $^{3}J_{HH}$ 1.6 Hz), 7.84 d (1H, CH=C<u>H</u>, $^{3}J_{HH}$ 1.6 Hz), 8.11 d (1H, =CH, $^{3}J_{PH}$ 14.3 Hz). ^{13}C NMR spectrum (CD_3OD, 100.61 MHz), δ_C, ppm: 22.96, 23.02, 23.06 and 23.18 [$(\underline{C}H_3)_2CH$], 35.08 (CH_3N), 72.88 d [$(CH_3)_2\underline{C}HOP$, $^{3}J_{PC}$ 5.4 Hz], 115.45 d (=CP, $^{1}J_{PC}$ 197.9 Hz), 123.35, 125.69 ($CH_3N\underline{C}H$=), 126.05, 127.57 (=NCH=), 135.74 d (C=<u>C</u>H, $^{2}J_{PC}$ 8.7 Hz), 153.59, 153.80 (SC=N). ^{31}P NMR spectrum (CD_3OD, 161.98 MHz): δ_P 8.12 ppm. Mass spectrum: *m*/*z* 417.03479 $[M + H]^+$ (calculated for $C_{16}H_{25}N_4O_3PS_2$: *M* 416.4984).

^{1}H, ^{13}C, ^{31}P, and ^{15}N NMR spectra were recorded with a Bruker Avance 400 spectrometer. ESI high resolution mass spectra were registered with a Bruker MicrOTOF (temperature of the ionizing chamber 180°C, ionization voltage 70 or 100 eV).

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