ISSN 1070-3632, Russian Journal of General Chemistry, 2015, Vol. 85, No. 2, pp. 500–501. © Pleiades Publishing, Ltd., 2015.
Original Russian Text © D.V. Lyamenkova, N.B. Viktorov, A.V. Dogadina, 2015, published in Zhurnal Obshchei Khimii, 2015, Vol. 85, No. 2, pp. 330–332.

LETTERS TO THE EDITOR

To the 80th Anniversary of B.I. Ionin

3-Phosphorylated 2*H*-Azirines

D. V. Lyamenkova, N. B. Viktorov, and A. V. Dogadina

St. Petersburg State Technological Institute (Technical University),
Moskovskii pr. 26, St. Petersburg, 190013 Russia
e-mail: dog_alla@mail.ru

Received November 27, 2014

Keywords: chloroethynylphosphonate, azirine, phosphorylated azirine

DOI: 10.1134/S1070363215020243

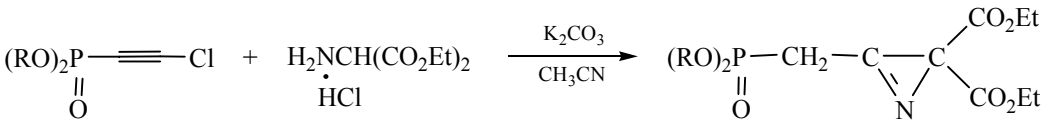
Earlier systematic investigations of chloroacetylenephosphonates reactions with conventional CH-acids performed in our research group have discovered regularities and synthetic potential of the process. In particular, the reaction with malonic acid derivatives leads to formation of the substitution–addition products [1], whereas in the cases of acetylacetone [2], ethyl acetoacetate [3, 4], and their analogs the reaction occurs exclusively via substitution of the chlorine atom with preservation of the triple bond. Reactions of chloroacetylenephosphonates with amidomalonates proceed via substitution followed by cyclization involving the carbonyl group oxygen and yielding phosphorylated oxazolines [5].

In the present work we report our latest results on study of the reaction of equimolar amounts of chloroethynylphosphonate and diethyl aminomalonate hydrochloride. The reaction of equimolar amounts of the substrates proceeded in anhydrous acetonitrile medium in the presence of excess of K_2CO_3 at room temperature to afford new 3-phosphorylated 2*H*-azirines **I–III** in 85–95% yield. Formation of the phosphorylated azirines occurred as substitution of the chlorine atom in chloroethynylphosphonate with aminomalonate anion followed by cyclization via attack of the nucleophilic amino group at the same acetylene carbon atom (Scheme 1).

Azirines **I–III** are viscous light-yellow liquids readily soluble in chloroform, benzene, and alcohols. Structures of azirines **I–III** were elucidated by means of ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy. In detail, characteristic signals of the malonate ethoxy groups were observed in the ^{1}H NMR spectra along with the signals of alkoxy fragments of the phosphoryl group and the doublet signal of the methylene group showing characteristic constant of spin-spin coupling with phosphorus nuclei of ≈20 Hz. The ^{13}C NMR spectra contained a strong-field signal of methylene carbon atom with typical spin-spin coupling constant $^1J_{CP}$ of ≈140 Hz. Carbon atom of C=N bond gave the rise to a downfield doublet signal shifted to δ_C 145 ppm with spin-spin coupling constant $^2J_{CP}$ of 12 Hz. Carbonyl carbon atoms of the malonate fragment resonated as two singlet signals at δ_C 160 ppm. Chemical shift of the phosphorus nuclei of the prepared azirines was found at δ_P 19–22 ppm.

Noteworthy, formation of 3-phosphorylated 2*H*-azirines from phosphorylated vinyl azides was

Scheme 1.



I–III

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

observed upon photolysis (in 96–97% yield) and upon thermolysis (along with the corresponding oxaphospholenes) [6]. Regioisomeric phosphorylated 2*H*-azirines, structurally similar to azirines **I**–**III**, were prepared by the Austrian researches via three-step synthesis from allylic α- and γ-hydroxyphosphonates via azides formation and their subsequent cyclization [7]; those azirines were synthesized by V.K. Brel, follower of professor B.I. Ionin via thermolysis of 2-azido-1,3-alkadiene- and 2-(4,5-dihydroisooxazole-5-yl)-2-azidoethenephosphonates as well [8].

3-(Dimethylphosphoryl)methyl-2,2-di(ethoxycarbonyl)-2*H*-azirine (I). A mixture of 0.01 mol of dimethyl chloroethynephosphonate, 0.01 mol of diethyl aminomalonate hydrochloride, and 0.025 mol of anhydrous K_2CO_3 in 25 mL of anhydrous acetonitrile was stirred at room temperature during 18 h. Precipitated inorganic salts were filtered off. The filtrate was evaporated, and the residue (pale yellow oily substance) was purified by column chromatography on silica gel, eluting with a 10 : 1 methylene chloride–methanol mixture. Yield 96%, R_f 0.44 (CH_2Cl_2–MeOH, 9 : 1). ^{1}H NMR spectrum ($CDCl_3$, 400.13 MHz), δ, ppm: 1.26 t (3H, $OCH_2C\underline{H}_3$, $^3J_{HH}$ 7.3 Hz), 1.36 t (3H, $OCH_2C\underline{H}_3$, $^3J_{HH}$ 7.1 Hz), 3.23 d (2H, $C\underline{H}_2P$, $^2J_{PH}$ 21.3 Hz), 3.71 d (6H, $C\underline{H}_3OP$, $^3J_{PH}$ 11.0 Hz), 4.24 q (2H, $OC\underline{H}_2CH_3$, $^3J_{HH}$ 7.3 Hz), 4.41 q (2H, $OC\underline{H}_2CH_3$, $^3J_{HH}$ 7.1 Hz). ^{13}C NMR spectrum ($CDCl_3$, 100.61 MHz), δ_C, ppm: 14.15, 14.51 ($CH_2\underline{C}H_3$), 26.26 d ($\underline{C}H_2P$, $^1J_{PC}$ 142.4 Hz), 52.93 d ($\underline{C}H_3OP$, $^2J_{PC}$ 6.1 Hz), 60.83, 69.31 ($O\underline{C}H_2CH_3$), 107.42 (C–N), 145.17 d (C=N, $^2J_{PC}$ 12.1 Hz), 160.92, 161.33 (C=O). ^{31}P NMR spectrum ($CDCl_3$, 161.98 MHz): δ_P 22.0 ppm. Mass spectrum: *m*/*z* 330.0722 $[M + Na]^+$ (calculated for $C_{11}H_{18}NO_7P$: *M* 307.0821).

3-(Diethylphosphoryl)methyl-2,2-di(ethoxycarbonyl)-2*H*-azirine (II) was prepared similarly. Yield 91%, viscous pale yellow oil. ^{1}H NMR spectrum ($CDCl_3$, 400.13 MHz), δ, ppm: 1.24 t and 1.26 t (6H, $OCH_2C\underline{H}_3$, $^3J_{HH}$ 7.0 Hz), 1.32 t and 1.36 t (6H, $OCH_2C\underline{H}_3$, $^3J_{HH}$ 7.1 Hz), 3.28 d (2H, $C\underline{H}_2P$, $^2J_{PH}$ 20.3 Hz), 4.11 dq (4H, $C\underline{H}_2OP$, $^3J_{HH}$ 7.0, $^3J_{PH}$ 11.5 Hz), 4.30 q (2H, $OC\underline{H}_2CH_3$, $^3J_{HH}$ 7.1 Hz), 4.45 q (2H, $OC\underline{H}_2CH_3$, $^3J_{HH}$ 7.1 Hz). ^{13}C NMR spectrum ($CDCl_3$, 100.61 MHz), δ_C, ppm: 14.27, 14.71 ($CH_2\underline{C}H_3$), 15.93, 16.17 ($CH_2\underline{C}H_3$), 27.32 d ($\underline{C}H_2P$, $^1J_{PC}$ 141.4 Hz), 62.65 d ($\underline{C}H_2OP$, $^2J_{PC}$ 6.5 Hz), 63.41, 69.93 ($O\underline{C}H_2CH_3$), 107.51 (C–N), 145.66 d (C=N, $^2J_{PC}$ 12.1 Hz), 161.17, 161.48 (C=O). ^{31}P NMR spectrum ($CDCl_3$, 161.98 MHz), δ_P: 20.2 ppm. Mass spectrum: *m*/*z* 358.1032 $[M + Na]^+$ (calculated for $C_{13}H_{22}NO_7P$: *M* 335.1134).

3-(Diisopropylphosphoryl)methyl-2,2-di(ethoxycarbonyl)-2*H*-azirine (III) was prepared similarly. Yield 85%, viscous pale yellow oil. R_f 0.52 (CH_2Cl_2–MeOH, 10 : 1). ^{1}H NMR spectrum ($CDCl_3$, 400.13 MHz), δ, ppm: 1.13 t and 1.15 t (6H, $OCH_2C\underline{H}_3$, $^3J_{HH}$ 7.1 Hz), 1.18 d and 1.20 d [12H, $OCH(C\underline{H}_3)_2$, $^3J_{HH}$ 6.6 Hz], 3.11 d (2H, CH_2P, $^2J_{PH}$ 21.2 Hz), 4.28 q (2H, $OC\underline{H}_2CH_3$, $^3J_{HH}$ 7.1 Hz), 4.42 q (2H, $OC\underline{H}_2CH_3$, $^3J_{HH}$ 7.1 Hz), 4.63 m (2H, CHOP, $^3J_{HH}$ 6.6, $^3J_{PH}$ 11.5 Hz). ^{13}C NMR spectrum ($CDCl_3$, 100.61 MHz), δ_C, ppm: 14.32, 14.71 ($CH_2\underline{C}H_3$), 23.43, 23.53 ($CH\underline{C}H_3$), 28.14 d (CH_2P, $^1J_{PC}$ 142.3 Hz), 60.41, 69.52 ($O\underline{C}H_2CH_3$), 71.24 d (CHOP, $^2J_{PC}$ 6.4 Hz), 107.07 (C–N), 145.62 d (C=N, $^2J_{PC}$ 12.0 Hz), 160.96, 161.14 (C=O). ^{31}P NMR spectrum ($CDCl_3$, 161.98 MHz), δ_P: 19.0 ppm. Mass spectrum: *m*/*z* 386.1351 $[M + Na]^+$ (calculated for $C_{15}H_{26}NO_7P$: *M* 363.1447).

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

ACKNOWLEDGMENTS

This work was financially supported by Russian Foundation for Basic Research (project no. 13-03-00111-a).

REFERENCES

1. Didkovskii, N.G., *Cand. Sci. (Chem.) Dissertation*, St. Petersburg, 2007; Shekhadeh, A., Didkovskii, N.G., Dogadina, A.V., and Ionin, B.I., *Russ. J. Gen. Chem.*, 2005, vol. 75, no. 1, p. 9. DOI: 10.1007/s11176-005-0163-8.
2. Petryanina, A.I., Didkovskii, N.G., Dogadina, A.V., and Ionin, B.I., *Russ. J. Gen. Chem*., 2006, vol. 76, no. 9, p. 1516. DOI: 10.1134/S1070363206090271.
3. Khramchikhin, V.A., Yacobson, G.V., Dogadina, A.V., Khramchikhin, A.V., and Ionin, B.I., *Russ. J. Gen. Chem*., 2010, vol. 80, no. 2, p. 364. DOI: 10.1134/S1070363210020301.
4. Khramchikhin, V.A., Didkovskii, N.G., Khramchikhin, A.V., Dogadina, A.V., and Ionin, B.I., *Russ. J. Gen. Chem*., 2011, vol. 81, no. 8, p. 635. DOI: 10.1134/S1070363211080093.
5. Khramchikhin, V.A., Dogadina, A.V., Khramchikhin, A.V., and Ionin, B.I., *Russ. J. Gen. Chem*., 2012, vol. 82, no. 4, p. 776. DOI: 10.1134/S1070363212040299.
6. Abramovitch, R.A., Konieczny, M., Pennington, W., Kanamathareddy, S., and Vedachalam, V., *J. Chem. Soc. Chem. Commun*., 1990, no. 3, p. 269. DOI: 10.1039/C39900000269.
7. Öhler, E., and Kanzler, S., *Lieb. Ann. Chem*., 1994, no. 8, p. 867. DOI: 10.1002/jlac.199419940904.
8. Brel, V.K., *Synthesis*, 2007, no. 17, p. 2674. DOI: 10.1055/s-2007-983837.