ISSN 1070-3632, Russian Journal of General Chemistry, 2015, Vol. 85, No. 2, pp. 462–466. © Pleiades Publishing, Ltd., 2015.
Original Russian Text © Yu.G. Trishin, V.I. Namestnikov, 2015, published in Zhurnal Obshchei Khimii, 2015, Vol. 85, No. 2, pp. 289–293.

To the 80th Anniversary of B.I. Ionin

Synthesis of Tricyclic Spirophosphoranes via Reaction of 2-(4,5-Dihydrofuran-3-yl)-*N*-phenyl-1,3,2-oxazaphospholidine with *C*,*N*-Diarylnitrile Imines

Yu. G. Trishin and V. I. Namestnikov

St. Petersburg State Technological University of Plant Polymers,
ul. Ivana Chernykh 4, St. Petersburg, 198095 Russia
e-mail: trish@YT4470.spb.edu

Received December 29, 2014

Abstract—Unique tricyclic compounds with a five-coordinate phosphorus atom shared by three rings, 7-aryl-3′,5-diphenyl-3,5-dihydro-2*H*-spiro[1,2-oxaphospholo[2,3-*d*][1,2,4]diazaphosphinine-8,2′-[1,3,2]oxazaphospholidines], have been synthesized for the first time via reaction of 2-(4,5-dihydrofuran-3-yl)-3-phenyl-1,3,2-oxazaphospholidine with *C,N*-diarylnitrile imines. Presumably, these compounds are formed via a three-step process including generation of P^+–C=N–N^- dipolar ion, intramolecular N^-→C= cyclization with simultaneous opening of the dihydrofuran ring, and closure of oxaphospholane ring.

Keywords: phosphorus heterocycle, spirophosphorane, 4,5-dihydrofuran, nitrile imine

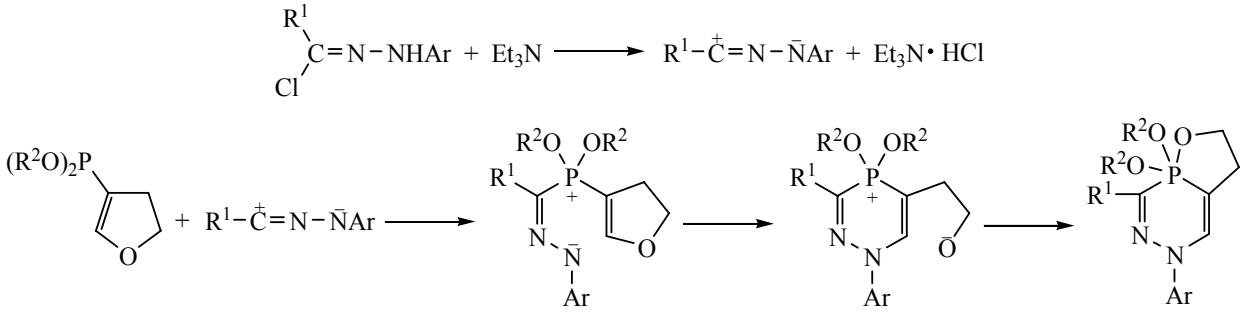
DOI: 10.1134/S1070363215020176

Reactions of α,β-unsaturated phosphorus(III) compounds with nitrile imines that are typical Huisgen 1,3-dipoles often lead to formation of six-membered phosphorus-containing heterocycles, 1,2,4-diazaphosphinines [1]. These reactions are regarded as multistep processes including nucleophilic addition of P(III) derivative to the electron-deficient atom of nitrile imine and intramolecular cyclization of the resulting dipolar ion. If a nucleofuge group (halogen atom, alkylsulfanyl or alkoxy group) is present in the position 2 of the alkenyl substituent attached to P(III), the cyclization step occurs as nucleophilic vinylic substitution of that group, and the double C=C bond is retained in the new ring.

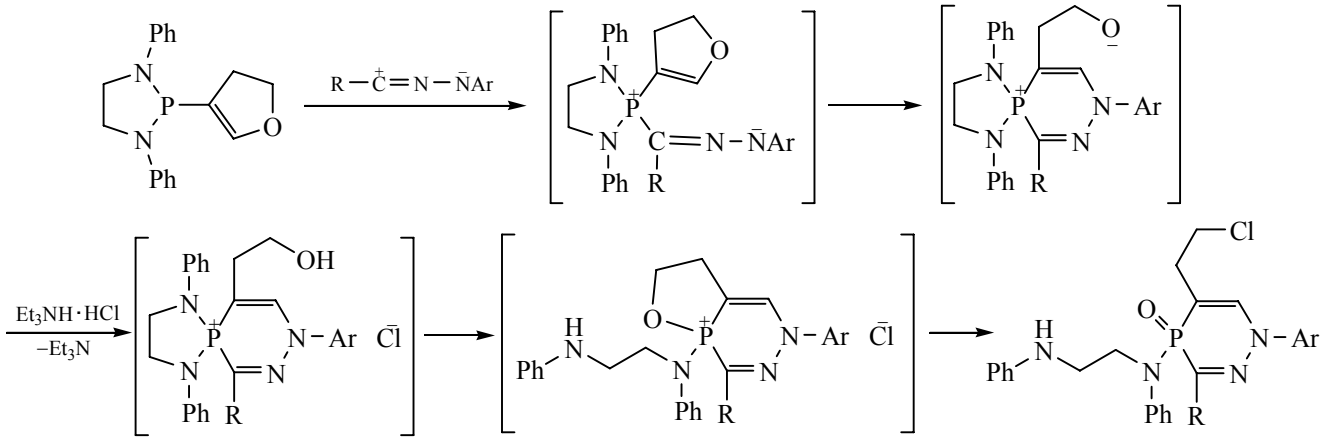
4,5-Dihydrofurans having P(III)-containing groups with the phosphorus atom attached to C^3 may be regarded as cyclic structural and electronic analogs of β-alkoxy-α,β-unsaturated P(III) derivatives. Indeed, we have shown that in the course of these compounds reactions with nitrile imines, cyclization of the intermediate dipolar ion P^+–C=N–N^- is always accompanied by opening of the dihydrofuran ring at the C–O bond [2–5], by analogy with elimination of alkoxy group in β-alkoxy-α,β-unsaturated P(III) compounds [6]. The reactions of nitrile imines with 4,5-dihydrofuran containing a dialkoxy-λ^3-phosphanyl group at C^3 have given stable bicyclic products with a five-coordinate phosphorus atom having a trigonal–bipyramidal configuration in the bridgehead position [2, 3]. Their formation involves two main steps: closure of 1,2,4-diazaphosphinine ring with simultaneous opening of the dihydrofuran ring and closure of the second P,O-containing ring of the bicyclic system as a result of the anionic oxygen atom attack at the quaternary phosphorus atom of the dipolar ion P^+–C–C–C–O^- (Scheme 1).

It may be presumed that analogous reaction of nitrile imines with 3-phosphorylated 4,5-dihydrofurans in which the phosphorus-containing group is a 1,3,2-diazaphospholidine or 1,3,2-oxazaphospholidine heterocycle rather than dialkoxyphoshanyl group should yield tricyclic spirophosphoranes, interesting objects of structural chemistry of organophosphorus compounds. The possibility for formation of such compounds is supported by the fact that 1,2-azaphospholidines react with some electrophiles (hexafluoroacetone, α,α,α-

Scheme 1.



Scheme 2.



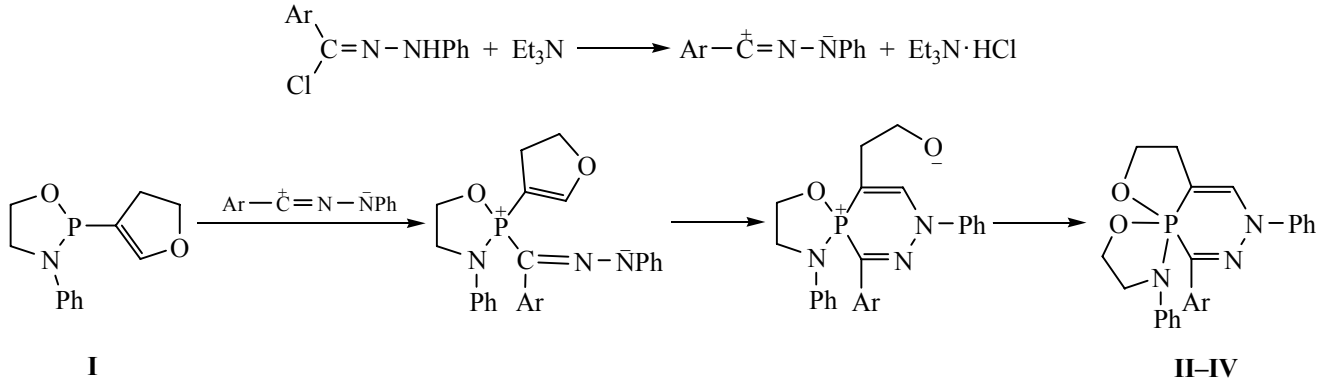
trifluoroacetophenone, or phenanthrenequinone) to afford fairly stable spirophosphoranes [7]. However, we have demonstrated that reactions of 2-(4,5-dihydrofuran-3-yl)-1,3-diphenyl-1,3,2-diazaphospholidine with nitrile imines are multistep processes involving opening of the both heterocycles (dihydrofuran and diazaphospholidine) in the starting organophosphorus substrate, which do not lead to spirophosphoranes [4, 5]. The final products are substituted 1,2,4-diazaphosphinines with a four-coordinate phosphorus atom (Scheme 2).

On the other hand, in the present work we found that replacement of the diazaphospholidine substituent in the 4,5-dihydrofuran molecule with oxazaphospholidine enabled preparation of the desired tricyclic spirophosphoranes. The reactions of 2-(4,5-dihydrofuran-3-yl)-3-phenyl-1,3,2-oxazaphospholidine (**I**) with *C*,*N*-diarylnitrile imines were carried out under mild conditions (in benzene or THF at 20°C), and nitrile imines were generated *in situ* by the action of triethylamine on the corresponding carbohydrazonoyl chlorides. We isolated unique tricyclic compounds with a five-coordinate spiro phosphorus atom, 7-aryl-3′,5-diphenyl-3,5-dihydro-2*H*-spiro[1,2-oxaphospholo-[2,3-*d*][1,2,4]diazaphosphinine-8,2′-[1,3,2]oxazaphospholidines] **II**–**IV** as final products (Scheme 3).

The path leading to compounds **II**–**IV** included (1) initial formation of the P^+–C=N–N^- dipolar ion, (2) attack of the anionic nitrogen atom at C^2 of the dihydrofuran ring (the latter being activated by the phosphonium group) leading to opening of the dihydrofuran ring via cleavage of the C–O bond and closure of the six-membered phosphorus-and-nitrogen-containing heteroring, and (3) closure of oxaphospholane ring as a result of interaction between the anionic oxygen atom and quaternary phosphorus atom of the P^+–C–C–C–O^- dipolar fragment. Thus, the described reaction involved formation of two new heterocycles, diazaphosphinine and oxaphospholane, the oxazaphospholidine ring of the initial P(III) compound being retained.

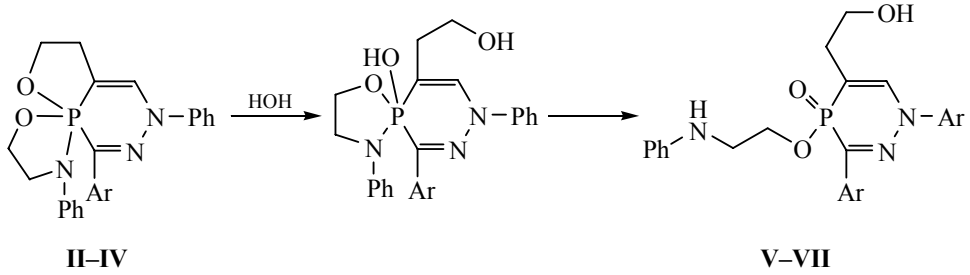
Tricyclic spirophosphoranes **II**–**IV** were light-yellow crystalline substances readily soluble in benzene, acetone, and THF and poorly soluble in diethyl ether.

Scheme 3.



Ar = Ph (**II**), *p*-$NO_2C_6H_4$ (**III**), *p*-BrC_6H_4 (**IV**).

Scheme 4.



They were extremely sensitive to hydrolysis. Exposure to atmospheric moisture (especially in solution) led to opening of the both five-membered rings and formation of 1,2,4-diazaphosphinine derivatives containing a four-coordinate phosphorus atom, 1,3-diaryl-5-(2-hydroxyethyl)-4-(2-phenylaminoethoxy)-1,4-dihydro-1,2,4λ^5-diazaphosphinine 4-oxides **V**–**VII** (Scheme 4).

Therefore, only 3′,5,7-triphenyl-3,5-dihydro-2*H*-spiro-[1,2-oxaphospholo[2,3-*d*][1,2,4]diazaphosphinine-8,2′-[1,3,2]oxazaphospholidine] (**II**) was isolated in analytically pure form containing more than 96% of the main substance (yield 52%, mp 189–190°C). Compounds **III** and **IV** were characterized by spectral methods. The purity of the isolated samples was 91 and 88%, respectively, according to the ^{1}H and ^{31}P NMR data (relative intensities of the 4-H signal in **II**–**IV** and 6-H signal in **V**–**VII**, respectively, as well as of the corresponding ^{31}P signals in the regions δ_P –74.5 to –76.0 ppm and 7.8–8.8 ppm).

Spirophosphoranes **II**–**IV** contained a signal at δ_P –74.5 to –76.0 ppm in the ^{31}P NMR spectra, typical of five-coordinate phosphorus atom and being the strongest evidence of the products tricyclic structure. The 4-H signal of **II**–**IV** appeared as a doublet at 6.51–6.55 ppm ($^3J_{PH}$ = 18.6–19.1 Hz) in the ^{1}H NMR spectra, methylene protons of the OCH_2 groups resonated as two pairs of multiplets at δ 3.41–3.45 and 4.24–4.33 ppm, the NCH_2 protons gave rise to two multiplets at δ 3.04–3.06 and 3.38–3.47 ppm, and a pair of multiplet signals at δ 2.24–2.27 and 2.68–2.70 ppm was assigned to the C^3H_2 group.

The hydrolysis products, substituted 1,2,4-diazaphosphinines **V**–**VII**, showed a signal at δ_P 7.8–8.8 ppm in the ^{31}P NMR spectra, typical of diazaphosphinine oxides with an exocyclic P–O bond [3, 8]. The 6-H proton of compounds **V**–**VII** resonated as a doublet at δ 7.70–7.75 ppm ($^3J_{PH}$ = 24.4–25.1 Hz) in the ^{1}H NMR spectra. The chemical shift and ^{1}H–^{31}P coupling constant were also typical of structurally related diazaphosphinines; on the other hand, the 6-H signal of **V**–**VII** was located in a weaker field than the 4-H signal of spirophosphoranes **II**–**IV**.

To conclude, unlike 2-(4,5-dihydrofuran-3-yl)-1,3-diphenyl-1,3,2-diazaphospholidine, the reaction of 3-phenyl-2-(4,5-dihydrofuran-3-yl)-1,3,2-oxazaphospholidine (**I**) with nitrile imines is not accompanied by

opening of the oxazaphospholidine ring. Presumably, this reaction path is favored by the formation of final products containing a five-coordinate phosphorus atom with trigonal–bipyramidal configuration which fits well geometry parameters of particular heterocycles constituting the tricyclic system and X–P–Y fragments (X, Y = C, O, N).

EXPERIMENTAL

^{1}H and ^{31}P NMR spectra were recorded with a Bruker Avance-400 spectrometer at 400.13 and 161.98 MHz, respectively, using $CDCl_3$ or C_6D_6 as solvent. The ^{31}P NMR chemical shifts were measured relative to 85% H_3PO_4. The elemental analyses were obtained using a Vario Microcube Elementar automatic CHNS analyzer; the phosphorus content was determined by spectrophotometry.

All operations during the synthesis and isolation of phosphorus(III) compounds and their further reactions were carried out in anhydrous solvents under argon.

2-(Phenylamino)ethanol (purity 99%) was a commercial product (from Acros Organics). Nitrile imines were generated *in situ* from the corresponding hydrazonoyl chlorides [9] by the action of triethylamine. Benzene, THF, diethyl ether, and triethylamine were purified and dried according to conventional procedures [10].

3-(Dichlorophosphanyl)-4,5-dihydrofuran was synthesized according to the procedure adopted from [3]. A suspension of 437 g (2.1 mol) of phosphorus pentachloride in 250 mL of benzene was cooled 10°C, 50 g (0.7 mol) of tetrahydrofuran was added under stirring, and the mixture was stirred during 1 h at 10°C and during 1 h at 20°C. The precipitate was filtered off, washed with benzene (100 mL), and dried under reduced pressure. We isolated 317 g (100%) of trichloro(4,5-dihydrofuran-3-yl)phosphonium hexachlorophosphate which was dispersed in 400 mL of benzene, and 360 g (1.4 mol) of tetraethylammonium iodide was added in small portions under stirring at 20°C. The mixture was stirred during 1 h at 20°C, the ammonium salt was filtered and washed with benzene (100 mL), the filtrate was evaporated, and the residue was distilled under reduced pressure. Yield 80 g (66.5%), bp 43–45°C (1 mmHg), n_D^{20} = 1.5660. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.85 m (2H, CH_2C=, $^3J_{HH}$ = 10.0, $^4J_{HH}$ = 1.7, $^3J_{PH}$ = 0.7 Hz), 4.37 t (2H, CH_2O, $^3J_{HH}$ = 10.0 Hz), 6.60 d.t (1H, CH=, $^4J_{HH}$ = 1.7, $^3J_{PH}$ = 3.2 Hz). ^{31}P NMR spectrum ($CDCl_3$): δ_P 155.0 ppm. The physical constants and spectral characteristics of the product were consistent with those reported in [3].

2-(4,5-Dihydrofuran-3-yl)-3-phenyl-1,3,2-oxazaphospholidine (I). A solution of 0.12 mol of 3-(dichlorophosphanyl)-4,5-dihydrofuran in 50 mL of benzene was added dropwise at 0–5°C to a solution of 0.12 mol of 2-(phenylamino)ethanol and 35 mL (10% excess) of triethylamine in 300 mL of benzene. The mixture was stirred during 0.5 h at 0°C and during 0.5 h at 20°C. The precipitate of triethylamine hydrochloride was filtered off and washed with benzene, the filtrate was evaporated, and the residue was washed with diethyl ether and dried under reduced pressure. Yield 75%, mp 75–77°C. ^{1}H NMR spectrum (C_6D_6), δ, ppm: 2.05–2.18 m (2H, =CCH_2), 2.79 m (2H, NCH_2), 3.67–3.97 m (4H, OCH_2), 6.56 m (1H, =CH), 6.82–7.29 m (5H, Ph). ^{31}P NMR spectrum ($CDCl_3$): δ_P 119.70 ppm. Found, %: C 61.30; H 6.05; P 13.20. $C_{12}H_{14}NO_2P$. Calculated, %: C 61.27; H 6.00; P 13.17.

3′,5,7-Triphenyl-3,5-dihydro-2*H*-spiro[1,2-oxaphospholo[2,3-*d*][1,2,4]diazaphosphinine-8,2′-[1,3,2]-oxazaphospholidine] (II). A solution of 0.002 mol of phospholidine **I** in 5 mL of benzene and 0.003 mol of triethylamine were added at 20°C to 0.002 mol of *N*-phenylbenzohydrazonoyl chloride in 5 mL benzene. The mixture was incubated during 24 h at 20°C upon intermittent stirring. Triethylamine hydrochloride was filtered off and washed with benzene. The solvent was removed; the residue was dissolved in 20 mL of diethyl ether; the solution was separated from the undissolved material via decanting and incubated at –10 to –15°C; and the precipitate was filtered off and dried. Yield 52%, mp 189–190°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.27 m and 2.68 m (2H, =CCH_2), 3.04 m and 3.47 m (2H, NCH_2), 3.45–4.30 m (4H, OCH_2), 6.52 d (1H, =CH, $^3J_{PH}$ = 18.6 Hz), 7.00–7.92 m (15H, Ph). ^{31}P NMR spectrum ($CDCl_3$): δ_P –74.5 ppm. Found, %: C 69.80; H 5.69; P 7.15. $C_{25}H_{24}N_3O_2P$. Calculated, %: C 69.92; H 5.63; P 7.21. After 10 days of exposure to air, spirophosphorane **II** underwent gradual hydrolysis with formation of substituted diazaphosphinine **V** (ratio **II**/**V** 77 : 23). Compound **V** displayed a signal at δ_P 8.80 ppm in the ^{31}P NMR spectrum. Apart from signals belonging to compound **II**, the ^{1}H NMR spectrum contained a signal at δ 7.70 ppm ($^3J_{PH}$ = 24.8 Hz) assigned to 6-H in **V**.

Compounds **III** and **IV** were synthesized in a similar way using tetrahydrofuran as solvent.

7-(4-Nitrophenyl)-3′,5-diphenyl-3,5-dihydro-2*H*-spiro[1,2-oxaphospholo[2,3-*d*][1,2,4]diazaphosphinine-8,2′-[1,3,2]oxazaphospholidine] (III). Yield 63% (9% of hydrolysis product **VI**). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.27 m and 2.70 m (2H, $=CCH_2$), 3.06 m and 3.39 m (2H, NCH_2), 3.41–4.24 m (4H, OCH_2), 6.55 d (1H, =CH, $^3J_{PH}$ = 19.1 Hz), 6.99–8.21 m (14H, H_{arom}). ^{31}P NMR spectrum ($CDCl_3$): δ_P –76.0 ppm. Compound **VI**: δ 7.75 ppm (0.1H, $^3J_{PH}$ = 25.1 Hz); δ_P 7.90 ppm.

7-(4-Bromophenyl)-3′,5-diphenyl-3,5-dihydro-2*H*-spiro[1,2-oxaphospholo[2,3-*d*][1,2,4]diazaphosphinine-8,2′-[1,3,2]oxazaphospholidine] (IV). Yield 71% (12% of hydrolysis product). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.24 m and 2.69 m (2H, $=CCH_2$), 3.04 m and 3.38 m (2H, NCH_2), 3.44–4.33 m (4H, OCH_2), 6.51 d (1H, =CH, $^3J_{PH}$ = 18.9 Hz), 6.95–7.95 m (14H, H_{arom}). ^{31}P NMR spectrum ($CDCl_3$): δ_P –75.30 ppm. Compound **VII**: δ 7.70 ppm (0.14H, $^3J_{PH}$ = 24.4 Hz); δ_P 7.8 ppm.

ACKNOWLEDGMENTS

The authors thank T.V. Gonchar for the assistance in performing experiments.

This study was financially supported by Russian Foundation for Basic Research (project no. 11-03-00 648).

REFERENCES

1. Trishin, Yu.G., Chistokletov, V.N., and Petrov, A.A., *Sov. Sci. Rev., Sect. B*, 1991, vol. 15, part 5, p. 1.
2. Namestnikov, V.I., Trishin, Yu.G., and Bel'skii, V.K., *Russ. J. Gen. Chem*., 1996, vol. 66, no. 8, p. 1367.
3. Trishin, Yu.G., Namestnikov, V.I., and Bel'skii, V.K., *Russ. J. Gen. Chem*., 1999, vol. 69, no. 5, p. 736.
4. Trishin, Yu.G., Namestnikov, V.I., and Bel'skii, V.K., *Russ. Chem. Bull., Int. Ed*., 2000, vol. 49, no. 1, p. 129. DOI: 10.1007/BF02499078.
5. Trishin, Yu.G., Namestnikov, V.I., and Gonchar, T.V., *Russ. Chem. Bull., Int. Ed*., 2005, vol. 54, no. 7, p. 1637. DOI: 10.1007/s11172-006-0016-6.
6. Platonov, A.Yu., Trostyanskaya, I.G., Kazankova, M.A., and Chistokletov, V.N., *Zh. Obshch. Khim*., 1982, vol. 52, no. 2, p. 268.
7. Ramirez, F., Patwardhan, A.V., Kugler, H.J., and Smith, C.P., *J. Am. Chem. Soc*., 1967, vol. 89, p. 6276. DOI: 10.1021/ja01000a051; Ramirez, F., Gubati, A.S., and Smith, C.P., *J. Am. Chem. Soc*., 1967, vol. 89, p. 6283. DOI: 10.1021/ja01000a052.
8. Namestnikov, V.I., Tamm, L.A., Trishin, Yu.G., and Chistokletov, V.N., *Zh. Obshch. Khim*., 1987, vol. 57, no. 6, p. 1412; Erofeeva, M.R., Trishin, Yu.G., and Chistokletov, V.N., *Zh. Obshch. Khim*., 1989, vol. 59, no. 9, p. 2146; Namestnikov, V.I., Trishin, Yu.G., Tamm, L.A., and Chistokletov, V.N., *Zh. Obshch. Khim*., 1990, vol. 60, no. 3, p. 510; Senyukh, S.M., Namestnikov, V.I., Trishin, Yu.G., and Chistokletov, V.N., *Zh. Obshch. Khim*., 1990, vol. 60, no. 8, p. 1926; Trishin, Yu.G., Afanasov, A.F., Litvinov, I.A., Naumov, V.A., and Chistokletov, V.N., *Zh. Obshch. Khim*., 1990, vol. 60, no. 11, p. 2446.
9. Huisgen, R., Seidel, M., Wallbillich, G., and Knupfer, H., *Tetrahedron*, 1962, vol. 17, nos. 1–2, p. 3. DOI: 10.1016/S0040-4020(01)99001-5.
10. Tietze, L.-F. and Eicher, T., *Reaktionen und Synthesen im organisch-chemischen Praktikum und Forschungslaboratorium*, Stuttgart: Georg Thieme, 1991, 2nd ed.