Chemistry of Natural Compounds, Vol. 50, No. 2, May, 2014 [Russian original No. 2, March–April, 2014]

REACTION OF (+)-CARVONE WITH SEVERAL HETARYLSULFENYL CHLORIDES AND PYRIDYLSELENYL CHLORIDE

I. V. Kuznetsov,[1] V. A. Startseva,[1] L. E. Nikitina,[1*] V. K. Osmanov,[2] A. V. Borisov,[2] Zh. V. Matsulevich,[2] and V. V. Klochkov[3]

New menthane-type derivatives were prepared via hetarylsulfenyl-chlorination reactions of (+)-carvone with 2-benzothiazolyl-, 4,6-dimethyl-2-pyrimidyl-, and 3-methoxycarbonyl-2-pyridylsulfenyl chlorides and 2-pyridylselenyl chloride.

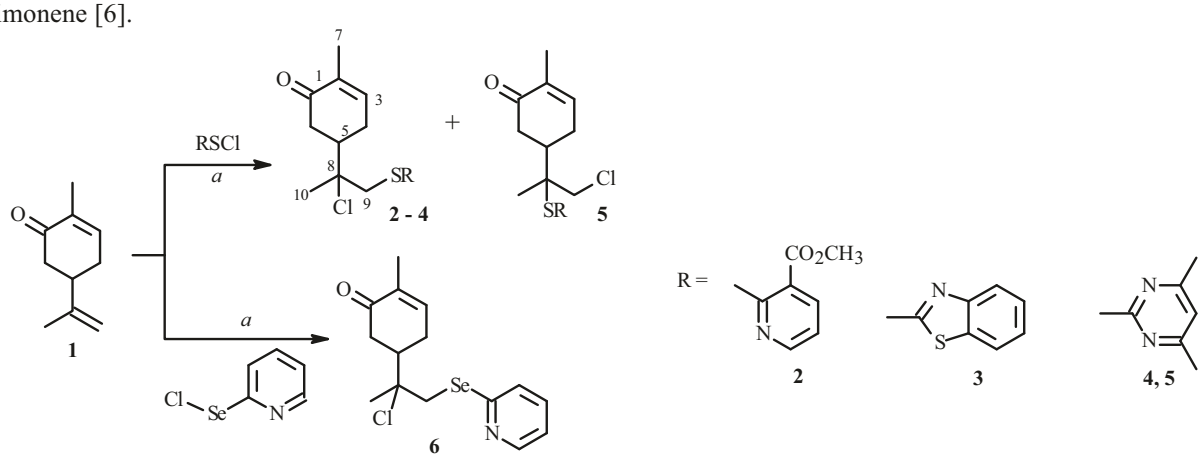
Keywords: (+)-carvone, hetarylsulfenyl-chlorination, monoterpenes.

One method for introducing sulfides into unsaturated compounds is to react olefins with sulfenyl chlorides, which forms primarily the 1,2-*trans*-addition products, *β*-halosulfides.

Reactions of olefins of various structures with hetarylsulfenyl and selenyl chlorides derived from pyridine, pyrimidine, and benzothiazole were reported [1–4]. The reactions of monoterpenes with heterocyclic sulfenyl chlorides are little studied with the exception of anecdotal studies on the sulfenyl-chlorination of 3-carene [5], *β*-pinene, and limonene [6]. The presence of three reactive centers in carvone provided an entry for reacting this terpene with various *S*-containing reagents. Electrophilic addition of thiols to carvone [7–12] and its sulfenyl-chlorination [13] were described before. However, its reactions with sulfenyl chlorides containing heterocyclic groups and selenyl-chlorination of monoterpenes have not been reported.

Herein we present results from a study of the functionalization of (+)-carvone (**1**) using sulfenyl chlorides comprising promising *N*-containing pharmacophores (3-methoxycarbonyl-2-pyridyl-, 2-benzothiazolyl-, and 4,6-dimethyl-2-pyrimidylsulfenyl chlorides) and the reaction of this monoterpene with 2-pyridylselenyl chloride. Sulfenyl chlorides and selenyl chloride were prepared by the published methods [14–16]. The structures of products isolated by column chromatography over silica gel were established using PMR, ^{13}C NMR, and ^{1}H–^{13}C HETCOR spectroscopy and GC-MS.

The *endo*-cyclic double bond of **1** was conjugated to a carbonyl, which diminished significantly its ability to react with electrophiles. Therefore, exclusively the *exo*-cyclic double bond of **1** underwent sulfenyl(selenyl)-chlorination, in contrast with limonene [6].



a. CH_2Cl_2, 25°C

1) Kazan State Medical University, 420012, Kazan′, Ul. Butlerova, 49, e-mail: valestar@mail.ru; 2) R. E. Alekseev Nizhnii Novgorod State Technical University, 603950, Nizhnii Novgorod, Ul. Minina, 24, e-mail: tantal@bmail.ru; 3) Kazan (Privolga) Federal University, 420008, Kazan′, Ul. Kremlevskaya, 18, e-mail: vladimir.klochkov@kpfu.ru. Translated from *Khimiya Prirodnykh Soedinenii*, No. 2, March–April, 2014, pp. 244–247. Original article submitted October 25, 2013.

 0009-3130/14/5002-0276

The reaction of **1** with 3-methoxycarbonyl-2-pyridylsulfenyl chloride was carried out at room temperature in CH_2Cl_2 with an equimolar ratio of reagents and without a catalyst. It formed the single product **2** even if an excess of sulfenyl chloride was used.

The PMR spectrum of **2** contained a broad singlet for the proton of the *endo*-cyclic double bond (6.73 ppm), a singlet for the OCH_3 protons (3.95 ppm), and resonances for protons of the pyridine ring (7.09, 8.21, 8.52 ppm) and terpene backbone (1.79–2.90 ppm). A feature of the PMR spectrum of **2** was the presence of a resonance for the C-8 methyl protons as two closely spaced singlets with the same intensity (1.61 and 1.62 ppm) in addition to a resonance for the thiomethylene group as two AB-systems with the same intensity and SSCC (3.70 ppm, 3.80, AB-system; 3.93, 4.03, A′B′-system; J = 16.0 Hz). The doubling of the number of C-8 methyl and thiomethylene lines was explained by the existence of **2** as a mixture of four stereoisomers with two diastereomers with 8*R*- and 8*S*-configurations in an ~1:1 ratio that were responsible for the observed pattern in the PMR spectrum and their two enantiomers with the 5*S*,8*S*- and 5*S*,8*R*-configurations. We observed previously a similar phenomenon for the reaction products of limonene 8,9-oxide with thiols and isothiuronium salts [17].

The proposed structure of **2** was confirmed by analyzing the two-dimensional $^1H–^{13}C$ HETCOR NMR experiment. The HETCOR spectrum had cross-peaks for the terpene at 1.80/15.0, corresponding to the 7-methyl; 2.17/27.6, 2.45/39.7, and 2.9/40.2, belonging to bound C–H atoms in the 4- and 6-positions; and 6.73/118.8, belonging to bound C–H atoms of the *endo*-cyclic double bond. The spectrum also showed cross-peaks for the pyridine at 7.09/139.2, 8.21/144.3, and 8.52/151.7. Resonances for bound C–H atoms at the asymmetric center (C-8) were doubled. Two cross-peaks at 1.61/27.1 and 1.62/27.1 corresponded to methyls of two diastereomers. Cross-peaks at 3.75/40.4 and 3.98/40.4 were due to correlation of bound C–H atoms in the 9-position.

The ^{13}C NMR spectrum also confirmed that **2** existed as a mixture of two pairs of enantiomers with different arrangements of the C-8 substituents. The spectrum showed a doubled set of C resonances. The C-8 resonance was located at 75.2 and 75.3 ppm, which indicated that it had a Cl atom, whereas C-9 (40.8 and 40.9 ppm) was bonded to a S atom.

The mass spectrum of **2** gave a peak with *m*/*z* 317 $[M – Cl]^+$ and fragments characteristic of the menthane system (*m*/*z* 121, 91, 79, 53).

(+)-Carvone was also reacted with this sulfenyl chloride using $LiClO_4$:nitromethane in order to produce possibly the cyclization product because it is known that $LiClO_4$ stimulates polar cycloaddition of hetarylsulfenyl chlorides to multiple bonds [4, 11]. The cyclization product was observed in the analogous reaction with (–)-pinene [6]. However, the reaction with **1** under these conditions formed only **2**.

The reaction of **1** with 2-benzothiazolylsulfenyl chloride under the same conditions (CH_2Cl_2, terpene:sulfenyl chloride, 1:1) also formed the single product **3** according to PMR, ^{13}C NMR, and $^1H–^{13}C$ HETCOR spectroscopy.

Also, the reaction of **1** with 4,6-dimethyl-2-pyrimidinylsulfenyl chloride formed the two regioisomers **4** and **5** that were characterized as an ~6:1 mixture.

The PMR spectrum of predominant regioisomer **4** contained a singlet for the *endo*-cyclic double bond proton (6.72 ppm), two AB-systems of thiomethylene protons from two pairs of enantiomers (3.68, 3.89, AB-system; 3.79, 4.01, A′B′-system; J = 12.0 Hz), and singlets for terpene backbone methyl protons (1.67 and 1.78). The PMR spectrum of minor isomer **5** showed a singlet for the *endo*-cyclic double bond proton (6.95 ppm), a quartet for the $–CH_2–Cl$ protons (4.38, J = 6.4 Hz), a singlet for the *endo*-cyclic double bond methyl protons (1.60), and a quartet for the C-8 CH_3 protons (1.75, J = 6.4 Hz). Spectra of **4** and **5** also had resonances for the thiazole protons as four multiplets (7.30, 7.42, 7.73, and 7.87 ppm) and for the other protons of the terpene backbone. The intensities of the C-8 methyl and methylene proton resonances were doubled because these compounds were mixtures of two pairs of enantiomers in an ~1:1 ratio. This was also confirmed by the ^{13}C NMR spectrum, in which resonances of each C atom consisted of two lines with similar chemical shifts.

Resonances for the $–CH_2–S–$ and $–CH_2–Cl$ groups of regioisomers **4** and **5** were assigned using data from the 2D $^1H–^{13}C$ NMR HETCOR experiment and the ^{13}C NMR spectrum. The region for correlation of bound C–H atoms in the 9-position of **4** and **5** had two cross-peaks in the $^1H–^{13}C$ HETCOR NMR spectrum at 3.78/41.0 and 3.91/41.0 for methylenes on the S atom of the two stereoisomers of main product **4**. Cross-peaks at 4.39/63.9 and 4.41/63.9 were assigned to methylenes on the Cl atom from the two stereoisomers of minor product **5**. The C-8 resonance in the ^{13}C NMR spectrum of main product **4** was located at 74.2 ppm; in the spectrum of minor isomer **5**, at 57.8 ppm. This indicated that this C atom was bonded to Cl in the predominant isomer.

The reaction of **1** with 2-pyridinylselenyl chloride formed a single addition product (**6**) at the *exo*-cyclic double bond according to the expanded Markovnikov rule.

The PMR spectrum of **6** had a singlet for the *endo*-cyclic double bond proton (6.71 ppm), a multiplet for the $–CH_2Se–$ group (3.87), singlets for protons of the two terpene backbone methyls (1.64 and 1.75), and multiplets for four pyridine protons (7.05, 7.32, 7.44, 8.44 ppm). The ^{13}C NMR spectrum showed a resonance at 75.5 ppm for the quaternary C-8 atom bound to Cl. Compound **6** existed as a mixture of the 8*R*- and 8*S*-stereomers according to PMR and ^{13}C NMR spectroscopy.

Thus, sulfenyl(selenyl) chlorides added in all studied reactions to the *exo*-cyclic double bond of **1** primarily according to the expanded Markovnikov rule.

Our previously published test results for the antifungal activity of a series of S-containing terpenoid derivatives of the carane-, pinane-, and menthane-types showed that individual menthane-type thioterpenes exhibited high antifungal activity [18–22].

The antifungal activity of the thioterpenoids with hetarylsulfide groups was studied using a disk-diffusion method on agar medium [23]. Unfortunately, all compounds possessed low levels of antifungal activity against both mold and mycelial fungi.

EXPERIMENTAL

The course of reactions and purity of products were monitored by TLC on Silufol UV-254 and Sorbfil plates (EtOH–H_2SO_4–anisaldehyde detector, 90:5:5). Preparative chromatography was performed over KSKG silica gel (0.10–0.16 μm, Ekofarm). We used D-(+)-carvone (Acros Organics). Solvents were purified and dried by the usual methods [24].

PMR and ^{13}C NMR spectra were recorded with HMDS internal standard on Bruker Avance 400 (operating frequency 400 and 100 MHz for ^1H and ^{13}C) and Varian Unity-300 (operating frequency300 MHz for ^1H) spectrometers. Chemical shifts were determined relative to resonances of residual protons in the deuterated solvent.

GC-MS was carried out on a DFS Thermo Electron Corp. (USA) instrument using electron-impact ionization, ionizing-electron energy 70 eV; ion-source temperature 280°C, DB-5MS Agilent capillary column (30 m × 0.254 mm), and He carrier gas flowing at 1 mL/min. Mass spectra were processed using the Xcalibur program. Samples were diluted in chromatographically pure C_6H_6 to a concentration of ~10^{-6} mol/μL before injection into the instrument. The sample volume was 1 μL.

General Method for Synthesizing Sulfenyl Chlorides from Disulfides. Disulfide (1 mmol) in CH_2Cl_2 (5 mL) was treated with a solution of sulfuryl chloride (1 mmol) in CH_2Cl_2 (5 mL) at 25–30°C and stirred for 2–5 min. The solvent was evaporated to afford sulfenyl chlorides that were used in the reactions with the terpenes.

Reaction of 1 with Sulfenyl Chlorides. Freshly prepared sulfenyl chloride (2 mmol) in CH_2Cl_2 (4 mL) at room temperature was stirred, treated with **1** (2 mmol) dissolved in CH_2Cl_2 (4 mL) (1:1 ratio of reagents), and stirred in a flask on a magnetic stirrer. The course of the reaction was monitored by TLC. When the reaction was finished (5–7 d), the solvent was evaporated (water aspirator). The reaction products were isolated by column chromatography over silica gel (*n*-hexane–CH_2Cl_2) as yellowish oils. Yield of **2**, 65%; **3**, 60%; **4** and **5**, 55%.

Methyl 2-{[2-Chloro-2-(4-methyl-5-oxocyclohex-3-en-1-yl)propyl]thio}pyridine-3-carboxylate (2). ^1H NMR spectrum (300 MHz, $CDCl_3$, δ, ppm, J/Hz): 1.61 and 1.62 (3H, s, H-10), 1.76 (3H, s, H-7), 2.17–2.90 (5H, m, H-4, 5, 6), 3.95 (3H, s, OCH_3), 3.70 and 3.80 – AB-system; 3.93 and 4.03 – A′B′-system (J = 16.0), 6.73 (1H, s, H-3), 7.09 (1H, m, H_{arom}), 8.21. (1H, m, H_{arom}), 8.52 (1H, m, H_{arom}). ^{13}C NMR spectrum (100 MHz, $CDCl_3$, δ, ppm): 15.8 (C-7), 27.1 (C-10), 27.6 (C-4), 39.7 (C-5), 40.2 (C-6), 40.8 (C-9), 52.5 (C-17), 75.2 (C-8), 118.8 (C-3), 122.9 (C-12), 135.3 (C-2), 139.2 (C-13), 144.3 (C-14), 151.7 (C-15), 160.4 (C-11), 165.5 (C-16), 199.1 (C-1). Mass spectrum, *m/z* (I_{rel},%): 317 $[M – Cl]^+$ (1), 284 (10), 256 (14), 234 (8), 220 (7), 208 (100), 202 (4), 182 (2), 167 (51), 148 (34), 138 (81), 121 (11), 111 (63), 91 (47), 79 (83), 67 (19), 53 (41).

5-[1-(1,3-Benzothiazol-2-ylthio)-2-chloropropan-2-yl]-2-methylcyclohex-2-en-1-one (3). ^1H NMR spectrum (400 MHz, $CDCl_3$, δ, ppm, J/Hz): 1.63 and 1.64 (3H, s, H-10), 1.73 (3H, s, H-7), 2.17–2.90 (5H, m, H-4, 5, 6), 2.40, 2.46 (each 3H, s, CH_3-arom), 3.92 and 4.08 – AB-system; 3.94 and 4.06 – A′B′-system (J = 13.68), 6.70 (2H, m, H-3, H_{arom}). ^{13}C NMR spectrum (100 MHz, $CDCl_3$, δ, ppm): 15.5 (C-7), 23.7 (C-15, C-16), 26.9 (C-10), 27.7 (C-4), 39.9 (C-6), 41.2 (C-9), 43.1 (C-5), 75.3 (C-8), 117.2 (C-14), 135.3 (C-2), 144.3 (C-3), 167.7 (C-12, C-13), 169.6 (C-11), 198.9 (C-1). Mass spectrum, *m/z* (I_{rel},%): 316 $[M – HCl]^+$ (1), 268 (100), 218 (8), 232 (72), 218 (20), 206 (80), 200 (68), 186 (16), 167 (69), 148 (20), 138 (88), 121 (12), 91 (50), 79 (78), 67 (18), 53 (42).

5-{2-Chloro-1-[(4,6-dimethylpyrid-2-yl)thio]propan-2-yl}-2-methylcyclohex-2-en-1-one (4). ^{1}H NMR spectrum (300 MHz, $CDCl_3$, δ, ppm, J/Hz): 1.68, 1.77 (each 3H, s, H-7, 10), 2.17–2.90 (5H, m, H-4, 5, 6), 3.68 and 3.89 – AB-system; 3.79 and 4.01 – A′B′-system (J = 12.0), 6.72 (1H, m, H-3), 7.30 (1H, m, H_{arom}), 7.42 (1H, m, H_{arom}), 7.73 (1H, m, H_{arom}), 7.87 (1H, m, H_{arom}). ^{13}C NMR spectrum (100 MHz, $CDCl_3$, δ, ppm): 15.6 (C-7), 26.9 (C-10), 27.6 (C-4), 39.7 (C-6), 39.7 (C-5), 41.0 (C-9), 74.2 (C-8), 121.1, 121.7, 124.6, 126.1 (C-13, C-14, C-15, C-16), 135.3 (C-2), 135.4 (C-17), 144.3 (C-3), 152.7 (C-12), 165.3 (C-11), 198.1 (C-1).

5-{1-Chloro-2-[(4,6-dimethylpyrid-2-yl)thio]propan-2-yl}-2-methylcyclohex-2-en-1-one (5). ^{1}H NMR spectrum (300 MHz, $CDCl_3$, δ, ppm, J/Hz): 1.60 (3H, s, H-7), 1.75 (3H, q, J = 6.4, H-10), 2.17–2.90 (5H, m, H-4, 5, 6), 4.38 (2H, q, J = 6.4, CH_2-Cl), 6.95 (1H, m, H-3), 7.30 (1H, m, H_{arom}), 7.42 (1H, m, H_{arom}), 7.73 (1H, m, H_{arom}), 7.87 (1H, m, H_{arom}). ^{13}C NMR spectrum (100 MHz, $CDCl_3$, δ, ppm): 16.6 (C-7), 23.6 (C-10), 29.7 (C-4), 39.7 (C-6), 39.7 (C-5), 63.9 (C-9), 57.8 (C-8), 121.1, 121.7, 124.6, 126.1 (C-13, C-14, C-15, C-16), 135.3 (C-2), 135.4 (C-17), 144.3 (C-3), 152.7 (C-12), 165.3 (C-11), 198.1 (C-1).

Reaction of 1 with 2-Pyridylselenyl Chloride. Crystalline 2-pyridylselenyl chloride (2 mmol) in CH_2Cl_2 (4 mL) at room temperature was stirred, treated with **1** (2 mmol) dissolved in CH_2Cl_2 (4 mL), and stirred for 15 d. When the reaction was finished, unreacted selenyl chloride was filtered off. The solvent was evaporated (water aspirator). Product **6** was isolated by column chromatography over silica gel (*n*-hexane–CH_2Cl_2, 60:40) as an odorless yellowish oil. Yield of **6**, 68%.

5-[2-Chloro-1-(2-pyridylseleno)propan-2-yl]-2-methylcyclohex-2-en-1-one (6). ^{1}H NMR spectrum (400 MHz, $CDCl_3$, δ, ppm, J/Hz): 1.64, 1.75 (each 3H, s, H-7, 10), 2.17–2.90 (5H, m, H-4, 5, 6), 3.87 (2H, m, $SeCH_2$), 4.77, 4.79 (each 1H, s, H-9), 6.71 (1H, s, H-3), 7.05 (1H, m, H_{arom}), 7.32 (1H, m, H_{arom}), 7.44 (1H, m, H_{arom}), 8.44 (1H, m, H_{arom}).^{13}C NMR spectrum (100 MHz, $CDCl_3$, δ, ppm): 15.6 (C-7), 27.6 (C-10), 27.7 (C-4), 37.4 (C-9), 39.8 (C-6), 43.3 (C-5), 75.7 (C-8), 120.8 (C-14), 125.6 (C-12), 135.3 (C-2), 136.2 (C-13), 144.3 (C-11), 149.9 (C-15), 153.4 (C-3), 199.1 (C-1).

Reaction of 1 with 3-Methoxycarbonyl-2-pyridylsulfenyl Chloride in $LiClO_4$–Nitromethane. A solution of freshly prepared 3-methoxycarbonyl-2-pyridylsulfenyl chloride (5 mmol) in nitromethane (10 mL) at 20°C was stirred and treated dropwise with $LiClO_4$ (5 mmol) in nitromethane (30 mL) and **1** (5 mmol) in nitromethane (10 mL). After 20 d, the reaction mixture was treated with CH_2Cl_2 (100 mL). The precipitate of LiCl and $LiClO_4$ was filtered off and rinsed multiple times with CH_2Cl_2. The filtrate was evaporated at reduced pressure. The solvent was removed to afford **2** by column chromatography over silica gel (*n*-hexane–CH_2Cl_2, 70:30) as a yellowish oil with a weak odor. Yield of **2**, 55%.

ACKNOWLEDGMENT

The work was performed under the auspices of state support of K(P)FU in order to increase its competency among the worldwide leading scientific and educational centers.

REFERENCES

1. A. V. Borisov, Zh. V. Matsulevich, V. K. Osmanov, G. N. Borisova, and E. V. Savihina, *Chem. Heterocycl. Compd.*, **43**, 525 (2007).
2. A. V. Borisov, V. K. Osmanov, G. N. Borisova, Zh. V. Matsulevich, and G. K. Fukin, *Mendeleev Commun.*, **19**, 49 (2009).
3. V. K. Osmanov, G. N. Borisova, G. V. Zatonskii, and A. V. Borisov, *Izv. Akad. Nauk, Ser. Khim.*, 2552 (2008).
4. V. K. Osmanov, G. N. Borisova, V. V. Kachala, and A. V. Borisov, *Izv. Akad. Nauk, Ser. Khim.*, 1260 (2010).
5. S. Rajesh, M. M. Reddy, and J. Iqbal, *Tetrahedron Lett.*, **37**, 7315 (1996).
6. I. V. Kuznetsov, L. E. Nikitina, and V. A. Startseva, *Khim. Interesakh Ustoich. Razvit.*, **19**, 217 (2011).
7. E. V. Sirazieva, V. A. Startseva, L. E. Nikitina, V. V. Plemenkov, V. V. Klochkov, and B. I. Khairutdinov, *Chem. Nat. Compd.*, **40**, 478 (2004).
8. A. T. Khan, S. Ghosh, and L. H. Choudhary, *Eur. J. Org. Chem.*, 2226 (2006).
9. K. P. Volcho, S. Yu. Kurbakova, E. V. Suslov, N. F. Salakhutdinov, A. V. Toktarev, G. V. Echevskii, and V. A. Barkhash, *J. Mol. Catal. A: Chem.*, **195**, 263 (2003).
10. P. Bakuzis and M. L. F. Bakuzis, *J. Org. Chem.*, **46**, 235 (1981).

11. A. T. Khan, S. Ghosh, and L. H. Choudhury, *Eur. J. Org. Chem.*, No. 9, 2226 (2006).
12. E. V. Sirazieva, V. A. Startseva, L. E. Nikitina, I. V. Kuznetsov, and V. V. Klochkov, *Chem. Nat. Compd.*, **42**, 693 (2006).
13. M. D. Bachi, Y. V. Bilokin, and A. Melman, *Tetrahedron Lett.*, **39**, 3035 (1998).
14. A. Toshimitsu, H. Owada, K. Terao, S. Uemura, and M. Okano, *J. Org. Chem.*, **49**, 3796 (1984).
15. D. N. Harp and P. Mathiaparanam, *J. Org. Chem.*, **37**, 1367 (1972).
16. P. Hamel, M. Girard, and N. N. Tsou, *J. Heterocycl. Chem.*, **36**, 643 (1999).
17. V. A. Startseva, L. E. Nikitina, and V. V. Plemenkov, *Russ. J. Org. Chem.*, **37**, 478 (2004).
18. L. E. Nikitina, V. A. Startseva, L. Yu. Dorofeeva, N. P. Artemova, I. V. Kuznetsov, S. A. Lisovskaya, and N. P. Glushko, *Chem. Nat. Compd.*, **46**, 28 (2010).
19. L. E. Nikitina, V. A. Startseva, I. A. Vakulenko, I. M. Khismatulina, S. A. Lisovskaya, N. P. Glushko, and R. S. Fassakhov, *Pharm. Chem. J.*, **43**, 251 (2009).
20. V. V. Gavrilov, E. N. Klimovitskii, V. A. Startseva, L. E. Nikitina, O. A. Lodochnikova, O. I. Gnezdilov, S. A. Lisovskaya, and N. I. Glushko, *Pharm. Chem. J.*, **44**, 126 (2010).
21. L. E. Nikitina, V. A. Startseva, N. P. Artemova, L. Yu. Dorofeeva, I. V. Kuznetsov, S. A. Lisovskaya, N. I. Glushko, and M. P. Kutyreva, *Pharm. Chem. J.*, **45**, 664 (2011).
22. V. A. Startseva, L. E. Nikitina, E. V. Sirazieva, L. Yu. Dorofeeva, S. A. Lisovskaya, N. I. Glushko, R. S. Garaev, and I. V. Akulina, *Khim. Interesakh Ustoich. Razvit.*, **17**, 539 (2009).
23. N. B. Gradova, E. S. Babusenko, and I. B. Gornova, *Laboratory Course in General Microbiology* [in Russian], DeLi Print, Moscow, 2004, 144 pp.
24. W. L. F. Armarego and C. L. L. Chai, *Purification of Laboratory Chemicals*, 6th Ed., Butterworth-Heinemann, Oxford, 2009, 760 pp.