ISSN 1070-4280, Russian Journal of Organic Chemistry, 2008, Vol. 44, No. 10, pp. 1512–1516. © Pleiades Publishing, Ltd., 2008.
Original Russian Text © O.V. Petrova, L.N. Sobenina, I.A. Ushakov, A.I. Mikhaleva, 2008, published in Zhurnal Organicheskoi Khimii, 2008, Vol. 44, No. 10, pp. 1534–1538.

Dedicated to Full Member of the Russian Academy of Sciences B.A. Trofimov on his 70th anniversary

Reaction of Indoles with Ethyl Bromopropynoate over Al_2O_3 Surface

O. V. Petrova, L. N. Sobenina, I. A. Ushakov, and A. I. Mikhaleva

Favorskii Irkutsk Institute of Chemistry, Siberian Division, Russian Academy of Sciences, ul. Favorskogo 1, Irkutsk, 664033 Russia
e-mail: ol_petr@irioch.irk.ru

Received June 9, 2008

Abstract—1*H*-Indole and 2-methyl-1*H*-indole reacted with ethyl 3-bromopropynoate over aluminum oxide to give mixtures of the corresponding ethyl 3-(1*H*-indol-3-yl)propynoates and ethyl 3,3-bis(1*H*-indol-3-yl)-acrylates, the latter prevailing.

DOI: 10.1134/S1070428008100199

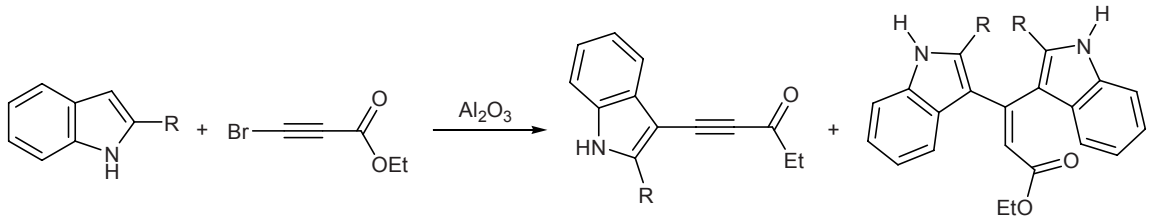
Development of effective procedures for functionalization of indole ring constitutes an important problem since compounds of the indole series are key building blocks for the synthesis of alkaloids and other biologically important heterocycles [1]. The most promising for subsequent modification are indole derivatives possessing exocyclic multiple bonds conjugated with the heteroaromatic ring, e.g., C-ethenyl- and C-ethynylindoles. Such compounds are widely used in organic synthesis, for example, as substrates in cycloaddition reactions with various reactive dienophiles [1, 2]. A large number of fused polynuclear heterocyclic systems can be obtained on their base, in particular derivatives of carbazole [3], indolylcarbazole [4], and β- and γ-carbolines [5], which exhibit a broad spectrum of biological activity [6] and are used as medical agents. Indole derivatives containing an acetylene fragment also possess high biological activity [7].

Most methods for the introduction into indole ring of substituents containing a triple bond are based on reactions of functionally substituted indoles with alkynes in the presence of palladium complexes, copper halides, and bases [5, 8, 9], as well as with copper acetylides [9]. Ethynylindoles are also formed via transformation of structural fragments directly attached to the indole ring [10]. Apart from the above methods [1, 11], ethynylindoles are often prepared by addition of indoles to alkynes [12] and replacement of functional groups [13] or hydrogen atom [14] in electrophilic alkenes. Such processes attract much interest, for they do not require preliminary functionalization of the heteroring.

We recently developed a convenient procedure for the introduction of an acetylenic fragment into pyrrole and indole ring via reaction with 1-acyl-2-bromoacetylenes over aluminum oxide at room temperature (reaction time 0.5–1 h) [15, 16]; this procedure requires no palladium or copper catalyst, base, and solvent, and preliminary functionalization of the heteroring is unnecessary. The cross coupling is accompanied by formation of 2-benzoyl-1,1-bis(pyrrol-2-yl)ethenes or 2-benzoyl-1,1-bis(indol-3-yl)ethenes as by-products whose yield does not exceed 6% [16]. Under analogous conditions, ethyl 3-bromopropynoate reacted with 1-unsubstituted and 1-vinyl-4,5,6,7-tetrahydro-1*H*-indoles over Al_2O_3 surface to give mixtures of the corresponding 2-benzoylethynyl-4,5,6,7-tetrahydro-1*H*-indoles and ethyl 3,3-bis(4,5,6,7-tetrahydro-1*H*-indol-2-yl)acrylates at a ratio of 2 : 1 [17].

With a view to extend our knowledge on the above cross coupling reaction, elucidate main factors determining the yield of products and their ratio, and obtain new indole derivatives having an exocyclic multiple bond conjugated with the ring, we examined reactions of 1*H*-indole (**Ia**) and 2-methyl-1*H*-indole (**Ib**) with ethyl 3-bromopropynoate (**II**) in the presence of aluminum oxide. The reaction was carried out by grinding

Scheme 1.



Ia, **Ib** **II** **IIIa**, **IIIb** **IVa**, **IVb**

R = H (**a**), Me (**b**).

the reactants with aluminum oxide, and its progress (conversion of the initial reactants and product ratio) was monitored by ^{1}H NMR spectroscopy. As we showed in [16], the major products in the reactions of indoles **Ia** and **Ib** with 3-bromo-1-phenylprop-2-yn-1-one where the corresponding (3-phenyl-3-oxoprop-1-yn-1-yl)indoles, while 3,3-bis(indolyl)-1-phenylprop-2-en-1-ones were formed as minor ones (5–6%) [16]. By contrast, ethyl 3-bromopropynoate (**II**) reacted with indoles **Ia** and **Ib** to give mainly the corresponding 3,3-bis(indolyl)acrylates **IVa** and **IVb** in up to 57% yield (Scheme 1), whereas ethynylindoles **IIIa** and **IIIb** were isolated in no more than 17% yield. Despite poor yield of the target products, the reaction was regioselective: only position *3* in the indole ring was involved.

It should be noted that ethyl 3-bromopropynoate (**II**) reacted with compounds **Ia** and **Ib** at a considerably lower rate than did 3-bromo-1-phenylprop-2-yn-1-one. According to the ^{1}H NMR data, the reaction of indole (**Ia**) with an equimolar amount of ester **II** in 2 h at room temperature produced only ~4% of ethynylindole **IIIa** and ~6% of acrylate **IVa**. By heating the reactant mixture for 1 h at 52–54°C (after grinding the reactants with aluminum oxide over a period of 15 min at room temperature), the concentration of acrylate **IVa** increased to 18–19%, the fraction of ethynylindole **IIIa** being 4–5%. Apart from products **IIIa** and **IVa**, the reaction mixture contained unreacted indole (**Ia**) and acetylenic ester **II**. In the presence of 2 equiv of the latter at room temperature the amount of ethynylindole **IIIa** increased to 20% in 1 h and to 26% in 3 h, and it was isolated in 17% yield (after 3 h). In this case, the concentration of acrylate **IVa** did not exceed 10%. When the reaction was carried out with 2 equiv of indole **Ia**, the yield of acrylate **IVa** reached 41%.

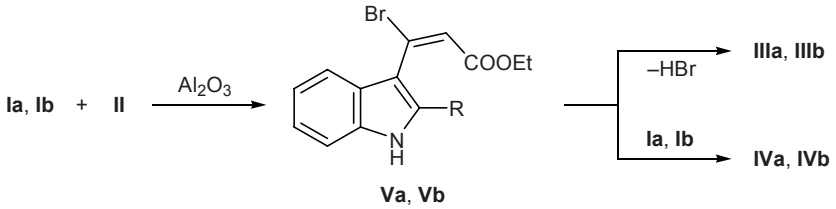
2-Methyl-1*H*-indole turned out to be more reactive than indole (**Ia**) toward ethyl 3-bromopropynoate (**II**): under comparable conditions (room temperature, equimolar amounts of the reactants) after 1 h, the reaction mixture contained only ~10% of initial indole **Ib**, while after 2 h only traces of **Ib** were detected. The corresponding ethynylindole **IIIb** and diindolylacrylate **IVb** were formed in approximately equal amounts. However, the product ratio changed after distillation of the mixture, and compounds **IIIb** and **IVb** were isolated in 12 and 57% yield, respectively.

We recently showed [18] that 2-phenylpyrrole reacts with 3-bromo-1-phenylprop-2-yn-1-one upon grinding the reactants with solid metal oxides to give either benzoylethynylpyrrole or product of pyrrole addition at the triple bond, depending on the metal oxide nature. We examined reactions of indoles **Ia** and **Ib** with ethyl 3-bromopropynoate (**II**) in the presence of other oxides, namely silicon dioxide, barium oxide, calcium oxide, magnesium oxide, and zinc oxide. Among these, only magnesium oxide showed a weak catalytic activity: according to the ^{1}H NMR data, only ~3–4% of ethynylindole **IIIa** and traces of acrylate **IVa** were present in the reaction mixture after 1 h at room temperature; after 24 h, the concentration of indole **IIIa** increased to 10–12%, and that of **IVa**, to 4–5%. Raising the temperature to 52–54°C accelerated the process: after 2 h, the reaction mixture contained 14–17% of compound **IIIa** and 5–7% of **IVa**.

As with Al_2O_3, the reaction of ethyl 3-bromopropynoate (**II**) with 2-methyl-1*H*-indole (**Ib**) over MgO surface was faster than with unsubstituted indole (**Ia**): after 1 h, the mixture contained 25% of **IIIb** and 20% of **IVb** (^{1}H NMR). The product ratio almost did not change when the reaction was prolonged to 4 h (26% of **IIIb** and 18% of **IVb**). In the presence of barium and calcium oxides, only 6–8% of cross-coupling product **IIIb** was formed, while traces of **IIIb** were detected in the reaction mixture obtained with the use of zinc oxide. In these cases, no diindolylacrylate **IVb** was formed.

When potassium carbonate was used as active surface in the reactions of indoles **Ia** and **Ib** with ethyl

Scheme 2.



3-bromopropynoate (**II**), the reaction mixture (in 1 h) contained neither expected products nor initial ester **II**, though potassium carbonate successfully promoted selective synthesis of 2-ethynyl-4,5,6,7-tetrahydroindoles [19]. Presumably, the ester group in **II** underwent base-catalyzed hydrolysis on exposure to atmospheric moisture to give potassium 3-bromopropynoate.

Indoles **Ia** and **Ib**, as well as pyrroles [15], are likely to react with acetylenic ester **II** through intermediate formation of ethyl 3-(1*H*-indol-2-yl)-3-bromoacrylates **Va** and **Vb**. Elimination of hydrogen bromide from the latter yields ethynylindoles **IIIa** and **IIIb**, while replacement of the bromine atom by the second indole molecule leads to bis(indolyl)acrylates **IVa** and **IVb** (Scheme 2), for compounds **IIIa** and **IIIb** failed to react with indole under the same conditions. Obviously, the rate of bromine replacement is higher than the rate of elimination of hydrogen bromide, so that compounds **IVa** and **IVb** are formed as the major products.

We can conclude that mild conditions and simple experimental procedure for the reaction of indoles with ethyl 3-bromopropynoate, as well as accessibility of the initial compounds, make the proposed method promising for one-step synthesis of indolylpropynoates and previously unknown diindolylacrylates.

EXPERIMENTAL

The IR spectra were recorded in KBr on a Bruker IFS-25 spectrometer. The ^{1}H and ^{13}C NMR spectra were measured on a Bruker DPX-400 instrument at 400.13 (^{1}H) and 100.6 MHz (^{13}C) relative to hexamethyldisiloxane as internal reference. Signals in the ^{1}H and ^{13}C NMR spectra were assigned with the aid of two-dimensional homo- (COSY, NOESY) and heteronuclear (HSQC, HMBC) correlation techniques.

Reaction of indoles Ia and Ib with ethyl 3-bromopropynoate (II) (*general procedure*). Ethyl 3-bromopropynoate (**II**), 0.09 g (0.51 mmol), was ground with aluminum, silicon, barium, calcium, magnesium, or zinc oxide or potassium carbonate (10-fold excess with respect to the overall weight of the reactants), 0.06 g (0.51 mmol) of indole (**Ia**) or 0.067 g (0.51 mmol) of indole (**Ib**) was added, and the mixture was ground over a period of 1 h in a porcelain mortar at room temperature. A 0.10–0.12-g sample of the mixture was withdrawn and treated with 1.5–2 ml of $CDCl_3$, and the solution was separated by filtration and analyzed by ^{1}H NMR spectroscopy; depending on the results, the reaction time was prolonged to 2–3 h. The reactions at 52–54°C were carried as follows. The reactants were ground over a period of 15 min at room temperature, the mixture was transferred into a glass beaker, and the beaker was immersed into a bath heated to the required temperature.

Ethyl 3-(1*H*-indol-3-yl)propynoate (IIIa). Indole, 0.06 g (0.51 mmol), was added in three portions to a mixture of 0.18 g (1.02 mmol) of ethyl 3-bromopropynoate and 2.40 g of Al_2O_3, and the mixture was intermittently ground in a porcelain mortar over a period of 3 h at room temperature. The mixture gradually turned pinkish–orange. It was transferred to a column charged with Al_2O_3, and the column was eluted with chloroform to isolate 0.018 g (17%) of compound **IIIa** and 0.004 g (5%) of **IVa**.

Compound **IIIa**. Light brown crystals, mp 100–102°C. IR spectrum, ν, cm^{-1}: 3268 (NH), 3052, 2978, 2922, 2855 (CH_2, Me), 2194 (C≡C), 1691 (C=O), 1661, 526, 1421, 1370, 1346, 1256, 1218, 1108, 1081, 1017, 744. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.36 t (3H, Me, J = 7.1 Hz), 4.30 q (2H, CH_2, J = 7.1 Hz), 7.24 m (2H, 5-H, 6-H), 7.40 d (1H, 7-H, J = 7.7 Hz), 7.60 d (1H, 2-H, J = 2.2 Hz), 7.77 d (1H, 4-H, J = 8.2 Hz), 8.93 br.s (1H, NH). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 14.2 (Me), 61.7 (OCH_2), 82.9, 84.1 (C≡C), 95.2 (C^3), 111.8 (C^7), 120.0 (C^4), 121.6 (C^5), 123.6 (C^6), 128.4 (C^{4a}), 132.4 (C^2), 135.1 (C^{7a}), 154.9 (CO). Found, %: C 73.42; H 5.12; N 6.47. $C_{13}H_{11}NO_2$. Calculated, %: C 73.23; H 5.20; N 6.57.

Ethyl 3,3-bis(1*H*-indol-3-yl)acrylate (IVa). A mixture of 0.12 g (1.02 mmol) of indole (**Ia**), 0.09 g (0.51 mmol) of ethyl 3-bromopropynoate, and 2.10 g

of Al_2O_3 was ground in a porcelain mortar over a period of 3 h at room temperature. The mixture was transferred to a column charged with Al_2O_3, and the column was eluted with chloroform. Yield 0.069 g (41%), light brown crystals, mp 210–212°C. IR spectrum, ν, cm^{-1}: 3392, 3302 (NH), 3117, 3058 (=CH), 2980, 2924, 2853 (CH_2, Me), 1683 (C=O), 1580, 1560, 1518, 1457, 1428, 1339, 1328, 1173, 1150, 1128, 1114, 1101, 1050, 1025, 847, 746. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.11 t (3H, Me, J = 7.1 Hz), 4.07 q (2H, CH_2, J = 7.1 Hz), 6.51 s (1H, CH=), 7.00 m (1H, 5-H), 7.05 d (1H, 2′-H, J = 2.4 Hz), 7.13 m (1H, 6-H), 7.15 m (1H, 5′-H), 7.22 m (1H, 6′-H), 7.24 d (1H, 2-H, J = 2.3 Hz), 7.29 d (1H, 4-H, J = 8.3 Hz), 7.32 d (1H, 7-H, J = 8.6 Hz), 7.36 d (1H, 7′-H, J = 8.5 Hz), 7.80 d (1H, 4′-H, J = 8.0 Hz), 8.40 br.s (1H, 1′-H), 8.55 br.s (1H, 1-H). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 14.2 (Me), 59.6 (OCH_2), 111.2 (C^7), 111.6 ($C^{7'}$), 112.6 (C^{α}), 115.4 (C^3), 119.5 ($C^{3'}$), 119.9 (C^5), 120.5 (C^4), 120.7 ($C^{4'}$), 121.0 ($C^{5'}$), 122.0 (C^6), 122.8 ($C^{6'}$), 125.5 ($C^{4a'}$), 126.2 (C^2), 127.3 (C^{4a}), 128.3 ($C^{2'}$), 135.8 (C^{7a}), 137.0 ($C^{7a'}$), 144.1 (C^{β}), 167.5 (CO). Found, %: C 76.54; H 5.20; N 8.50. $C_{21}H_{18}N_2O_2$. Calculated, %: C 76.34; H 5.49; N 8.48.

Ethyl 3-(2-methyl-1*H*-indol-3-yl)propynoate (IIIb) and ethyl 3,3-bis(2-methyl-1*H*-indol-3-yl)-acrylate (IVb). Ethyl 3-bromopropynoate, 0.133 g (0.75 mmol), was ground with 2.31 g of Al_2O_3, 0.098 g (0.75 mmol) of 2-methyl-1*H*-indole was added in three portions, and the mixture was intermittently ground in a porcelain mortar over a period of 2 h at room temperature. The mixture gradually turned orange. It was washed with 150 ml of diethyl ether, the solvent was removed, the residue (0.144 g of a dark brown crystalline material, a mixture of compounds **IIIb** and **IVb** at a ratio of 56:44 according to the ^{1}H NMR data) was dissolved in 3–4 ml of diethyl ether, and the light yellow crystals were filtered off, washed with diethyl ether, and dried. We thus isolated 0.058 g (43%) of compound **IVb**. The filtrate was applied to a column charged with Al_2O_3, and the column was eluted with chloroform to isolate 0.021 g (12%) of compound **IIIb** and 0.019 g (14%) of **IVb**. Overall yield of **IVb** 57%.

Compound **IIIb**. Light brown crystals, mp 136–138°C. IR spectrum, ν, cm^{-1}: 3334 (NH), 2964, 2924, 2853 (CH_2, Me), 2183 (C≡C), 1677 (C=O), 1461, 1367, 1256, 1232, 1158, 1027, 747, 735. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.36 t (3H, Me, J = 7.1 Hz), 2.58 s (3H, Me), 4.30 q (2H, CH_2, J = 7.1 Hz), 7.18 m (2H, 5-H, 6-H), 7.29 m (1H, 7-H), 7.68 d (1H, 4-H, J = 8.0 Hz), 8.20 br.s (1H, NH). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 13.1 (Me), 14.3 (H_2**Me**), 61.7 (OCH_2), 83.3 and 86.5 (C≡C), 93.5 (C^3), 111.0 (C^7), 119.6 (C^4), 121.5 (C^5), 123.0 (C^6), 129.2 (C^{4a}), 134.8 (C^{7a}), 144.8 (C^2), 155.2 (CO). Found, %: C 74.12; H 5.67; N 6.22. $C_{14}H_{13}NO_2$. Calculated, %: C 73.99; H 5.77; N 6.16.

Compound **IVb**. Light yellow crystals, mp 240–242°C. IR spectrum, ν, cm^{-1}: 3378, 3306 (NH), 3060 (=CH), 2977, 2930, 2875 (CH_2, Me), 1682 (C=O), 1582, 1558, 1530, 1485, 1456, 1427, 1368, 1326, 1288, 1256, 1187, 1142, 1034, 754, 740. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.11 t (3H, 2-Me, J = 7.1 Hz), 2.03 s (3H, 2′-Me), 2.15 s (3H, Me), 4.06 q (2H, CH_2, J = 7.1 Hz), 6.29 s (1H, CH=), 6.90 m (1H, 5-H), 7.03 m (2H, 5′-H, 6-H), 7.10 m (2H, 4-H, 6′-H), 7.26 m (2H, 7-H, 7′-H), 7.43 d (1H, 4′-H, J = 8.2 Hz), 7.96 br.s (1H, 1-H), 8.02 br.s (1H, 1′-H). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 12.4 (2-Me, 2′-Me), 14.3 (**Me**CH_2), 58.7 (CH_2), 110.5 ($C^{7'}$), 110.8 (C^7), 111.6 (C^3), 113.3 (C^{α}, $C^{3'}$), 118.4 (C^4, $C^{5'}$), 118.7 (C^5), 119.6 ($C^{4'}$), 120.2 (C^6), 120.8 ($C^{6'}$), 127.3 ($C^{4a'}$), 127.9 (C^{4a}), 135.2 (C^{7a}, $C^{7a'}$), 135.5 (C^2), 136.7 ($C^{2'}$), 145.1 (C^{β}), 165.9 (CO). Found, %: C 77.16; H 6.09; N 7.90. $C_{23}H_{22}N_2O_2$. Calculated, %: C 77.07; H 6.19; N 7.82.

REFERENCES

1. Sundberg, R.J., *The Chemistry of Indoles*, New York: Academic, 1970; *Comprehensive Organic Functional Group Transformations*, Katritzky, A.R., Meth-Cohn, O., and Rees, C.W., Eds., Oxford: Pergamon, 1995; Trofimov, B.A. and Nedolya, N.A., *Comprehensive Heterocyclic Chemistry III*, Katritzky, A.R., Ramsden, C.A., Scriven, E.F.V., and Taylor, R.J.K., Eds., Amsterdam: Elsevier, 2008, vol. 3, p. 45.
2. Gürtler, Ch.F., Steckhan, E., and Blechert, S., *J. Org. Chem*., 1996, vol. 61, p. 4136; Noland, W.E., Guang-Ming, X., Gee, K.R., Konkel, M.J., Wahlstrom, M.J., Condoluci, J.J., and Rieger, D.L., *Tetrahedron*, 1996, vol. 52, p. 4555; Trofimov, B.A., Sobenina, L.N., Demenev, A.P., and Mikhaleva, A.I., *Chem. Rev*., 2004, vol. 104, p. 2481.
3. Saroja, B. and Srinivasan, P.C., *Synthesis*, 1986, p. 748; Pindur, U. and Eitel, M., *Helv. Chim. Acta*, 1988, vol. 71, p. 1060; Hagiwara, H., Choshi, T., Nobuhiro, J., Fujimoto, H., and Hibino, S., *Chem. Pharm. Bull*., 2001, vol. 49, p. 881; Mohanakrishnan, A.K. and Balamurugan, R., *Tetrahedron Lett*., 2005, vol. 46, p. 4045.
4. Passarella, D., Giardini, A., Martinelli, M., and Silvani, A., *J. Chem. Soc., Perkin Trans. 1*, 2001, p. 127.
5. Zhang, H. and Larock, R.C., *J. Org. Chem*., 2002, vol. 67, p. 7048.

6. Aygün, A. and Pindur, U., *Synlett*, 2000, p. 1757; Rawat, M. and Wulff, W.D., *Org. Lett*., 2004, vol. 6, p. 329.
7. Cugola, A., Gaviraghi, G., and Micheli, F., WO Patent no. 94/20465, 1994; *Chem. Abstr*., 1994, vol. 121, no. 300763y; Hewkin, C.T., Di Fabio, R., Conti, N., Cugola, A., Gastaldi, P., Micheli, F., and Quaglia, A.M., *Arch. Pharm*., 1999, vol. 332, p. 55.
8. Passarella, D., Lesma, G., Deleo, M., Martinelli, M., and Silvani, A., *J. Chem. Soc., Perkin Trans. 1*., 1999, p. 2669; Hibini, S. and Choshi, T., *Nat. Prod. Rep*., 2002, vol. 19, p. 148; Soderberg, B.C.G., *Coord. Chem. Rev*., 2002, vol. 224, p. 171; Soderberg, B.C.G., *Coord. Chem. Rev*., 2003, vol. 241, p. 147.
9. Prikhod'ko, T.A., Kurilenko, V.M., Khlienko, Zh.N., Vasilevskii, S.F., and Shvartsberg, M.S., *Izv. Akad. Nauk SSSR, Ser. Khim*., 1990, p. 134.
10. Kamenskii, A.B., Smushkevich, Yu.I., Livshits, A.I., and Suvorov, N.N., *Khim. Geterotsikl. Soedin*., 1980, p. 959.
11. Joseph, B., Alagille, D., Rousseau, C., and Mérour, J.-Y., *Tetrahedron*, 1999, vol. 55, p. 4341; Pérez-Serrano, L., Casarrubios, L., Dominguez, G., González-Pérez, P., and Pérez-Castells, J., *Synthesis*, 2002, p. 1810; Yue, D., Yao, T., and Larok, R., *J. Org. Chem*., 2006, vol. 71, p. 62.
12. Lu, W., Jia, C., Kitamura, T., and Fujiwara, Y., *Org. Lett*., 2000, vol. 2, p. 2927; Oyamada, J., Lu, W., Jia, C., Kitamura, T., and Fujiwara, Y., *Chem. Lett*., 2002, vol. 31, p. 20; Zhang, Y., *Tetrahedron Lett*., 2005, vol. 46, p. 6483; Zhang, Y., *Tetrahedron*, 2006, vol. 62, p. 3917.
13. Hammadi, A., Menez, A., and Genet, R., *Tetrahedron Lett*., 1996, vol. 37, p. 3309; Selic, L. and Stanovnik, B., *Tetrahedron*, 2001, vol. 57, p. 3159.
14. Jia, C., Lu, W., Kitamura, T., and Fujiwara, Y., *Org. Lett*., 1999, vol. 1, p. 2097; Grimster, N.P., Gauntlett, C., Gogfrey, C.R.A., and Gaunt, M.J., *Angew. Chem., Int. Ed*., 2005, vol. 44, p. 3125; Capito, E., Brown, J.M., and Ricci, A., *Chem. Commun*., 2005, p. 1854.
15. Trofimov, B.A., Stepanova, Z.V., Sobenina, L.N., Mikhaleva, A.I., and Ushakov, I.A., *Tetrahedron Lett*., 2004, vol. 45, p. 6513; Trofimov, B.A., Sobenina, L.N., Stepanova, Z.V., Demenev, A.P., Mikhaleva, A.I., Ushakov, I.A., Vakul'skaya, T.I., and Petrova, O.V., *Russ. J. Org. Chem*., 2006, vol. 42, p. 1348; Trofimov, B.A., Sobenina, L.N., Stepanova, Z.V., Ushakov, I.A., Petrova, O.V., Tarasova, O.A., Volkova, K.A., and Mikhaleva, A.I., *Synthesis*, 2007, p. 447.
16. Sobenina, L.N., Demenev, A.P., Mikhaleva, A.I., Ushakov, I.A., Vasil'tsov, A.M., Ivanov, A.V., and Trofimov, B.A., *Tetrahedron Lett*., 2006, vol. 47, p. 7139.
17. Trofimov, B.A., Sobenina, L.N., Demenev, A.P., Stepanova, Z.V., Petrova, O.V., Ushakov, I.A., and Mikhaleva, A.I., *Tetrahedron Lett*., 2007, vol. 48, p. 4661.
18. Trofimov, B.A., Sobenina, L.N., Stepanova, Z.V., Vakul'skaya, T.I., Kazheva, O.N., Aleksandrov, G.G., Dyachenko, O.A., and Mikhaleva, A.I., *Tetrahedron*, 2008, vol. 64, p. 5541.
19. Trofimov, B.A., Sobenina, L.N., Stepanova, Z.V., Petrova, O.V., Ushakov, I.A., and Mikhaleva, A.I., *Tetrahedron Lett*., 2008, vol. 49, p. 3946.