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Dedicated to Full Member of the Russian Academy of Sciences M.G. Voronkov on his 90th anniversary

Highly Efficient Desilylation of 3-Trimethylsilylprop-2-ynamides by the Action of KF–Al_2O_3

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Abstract—A highly effective procedure has been developed for desilylation of 3-trimethylsilylprop-2-ynamides in the presence of KF–Al_2O_3 as catalyst. The corresponding terminal prop-2-ynamides were obtained in high yield in methanol at 25°C using 5 mol % of the catalyst (reaction time 20 min). Rise in temperature leads to the formation of *Z*,*E*-3-methoxyprop-2-enamides or 3,3-dimethoxypropanamides as a result of tandem desilylation–addition of methanol, depending on the conditions.

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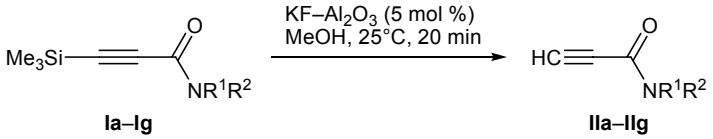
The synthetic strategy silylation–desilylation of triple bond is widely used in fine organic synthesis, in particular in total syntheses of highly efficient natural antibiotics [1]. This approach was partially reviewed in [2]. The presence of a trimethylsilyl group at triple C≡C bond stabilizes the latter so that it becomes inactive toward nucleophiles [3], organometallic compounds, and transition metal catalysts in various synthetic transformations [4]; as a result, regioselective cycloaddition of azides at the triple bond of various trimethylsilylalkynes becomes possible [5], the stability of compounds increases, and their solubility in organic solvents is improved.

Desilylation of acetylenic compounds can be performed with the use of various reagents, among which such bases as alkali metal hydroxides [6], alkoxides [7], and carbonates [8] in protophylic solvents, as well as potassium [9] and ammonium fluorides [10] are used most frequently. We recently showed that successful desilylation may be achieved with the aid of even weak bases generated in protic medium from metal oxides (PbO_2, MnO_2, Co_2O_3, Ni_2O_3) [11].

Despite diversity of desilylating agents, published data on desilylation of silicon-containing acetylenic compounds with an activated triple bond are few in number. Desilylation of such compounds requires mild conditions, taking into account the possibility for undesirable addition of alcohol or water (used as solvent) at the terminal triple bond in the resulting alkynes by the action of base in protophilic medium.

In the present work we developed an efficient procedure for desilylation of trimethylsilylacetylenes having an activated triple bond. 3-Trimethylsilylprop-2-ynamides **Ia**–**Ig** were selected as substrates, and KF–Al_2O_3, as reagent. Solid-phase desilylation of trimethylsilylalkynes under microwave irradiation required excess KF–Al_2O_3 (4 equiv) [12]. There are no published data on desilylation of trimethylsilylacetylene derivatives with an activated triple bond by the action of KF–Al_2O_3.

Scheme 1.



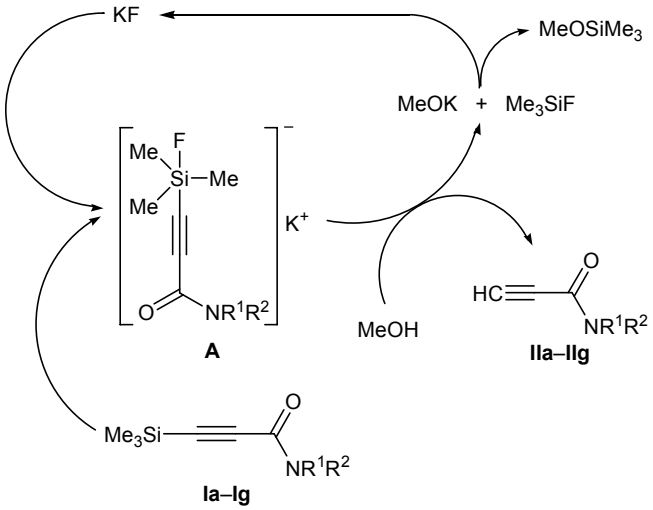
Ia–Ig **IIa–IIg**

R^1 = H, R^2 = H (**a**), Ph (**b**), $PhCH_2$ (**c**), 2,5-$Cl_2C_6H_3$ (**d**), 3-BrC_6H_4 (**e**), $HOCH_2CMe_2$ (**f**); R^1R^2N = morpholino (**g**).

In the reactions of amides **Ib**, **Id**, and **Ie** containing an aromatic ring with an equimolar amount of KF–Al_2O_3 in diethyl ether at room temperature the yield of the corresponding terminal propynamides did not exceed 62%. The efficiency of the process considerably increased when diethyl ether was replaced by methanol. Terminal propynamides **IIa**–**IIg** were isolated in high yield (82–99%) by the action of a catalytic amount of KF–Al_2O_3 (5 mol %) over a period of 20 min at room temperature (Scheme 1). *N*-(2-Hydroxy-1,1-dimethylethyl)prop-2-ynamide (**IIf**) was not reported previously. The developed procedure is advantageous due to selectivity of the reaction, experimental simplicity, mild conditions (room temperature), the use of a catalytic amount of desilylating agent, and purity of the products (no additional purification was necessary). The process was not accompanied by cleavage of the amide C–N bond and addition of methanol at the triple bond of the resulting terminal propynamide.

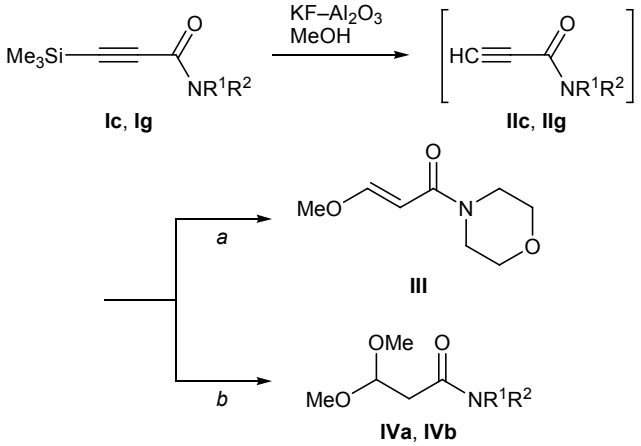
A probable scheme of KF–Al_2O_3-induced desilylation of trimethylsilylpropynamides **Ia**–**Ig** includes generation of complex **A** (Scheme 2) and its protonation with methanol to produce terminal propynamide, fluorotrimethylsilane, and potassium methoxide. Potassium fluoride liberated in the reaction of fluorotrimethylsilane with potassium methoxide returns to the catalytic cycle.

Scheme 2.



Rise in temperature favors tandem desilylation–methanol addition process with formation of previously unknown (*Z*,*E*)-3-methoxyprop-2-enamides (Scheme 3). By heating amides **Ic** and **Ig** in boiling methanol in the presence of KF–Al_2O_3 (5 mol %) over a period of 7 or 3 h, respectively, we obtained 3,3-dimethoxypropanamides **IVa** and **IVb** in high yield. The reaction of trimethylsilylpropynamide **Ig** with KF–Al_2O_3 (5 mol %) under microwave irradiation (700 W, 15 min) resulted in selective addition of one methanol molecule with formation of 88% of (*E*,*Z*)-4-(3-methoxyprop-2-enoyl)morpholine (**III**, *E*:*Z* = 1:2).

Scheme 3.



Ic, **IVa**, R^1 = H, R^2 = $PhCH_2$; **Ig**, **IVb**, R^1R^2N = morpholino; *a*: KF–Al_2O_3 (5 mol %), MeOH, microwave irradiation (700 W, 20 min) or KF–Al_2O_3 (12 mol %), MeOH–MeCN, reflux, 2 h; *b*: KF–Al_2O_3 (5 mol %), MeOH, reflux, 3–7 h.

Insofar as protodesilylation of various silicon-containing acetylenic amides occurs fairly readily, the efficiency of the tandem process is determined mainly by the stage of methanol addition at the terminal triple bond in intermediate propynamide. Higher reactivity of amide **Ig** in this process, as compared to *N*-benzyl analog **Ic**, may be rationalized in terms of higher basicity of benzylamine (pK_a 9.34 in water) as compared to morpholine (pK_a 8.70 in water) [13]. The use of a mixture of methanol with acetonitrile considerably inhibits methanol addition, and their ratio affects the reaction selectivity. According to the ^{1}H NMR data, amide **Ig** in boiling methanol (5 mol % of KF–Al_2O_3) is completely converted into 3,3-dimethoxypropanamide (**IVb**) in 3 h, whereas the reaction in MeOH–MeCN (1:2) gives a mixture of terminal propynamide **IIg** (14%), adduct **III** (66%), and dimethoxy derivative **IVb** (20%). Considerable reduction of the concentration of methanol (methanol–acetonitrile, 1:9) and increase in the catalyst concentration to 12 mol % ensures selective addition of methanol with formation of monomethoxy adduct **III** (*E*:*Z* = 1.0:1.2) in 88% yield on heating under reflux over a period of 2 h.

3-Methoxyprop-2-enamides may be regarded as push–pull vinyl ethers, while 3,3-dimethoxypropan-

amides are acetals derived from the corresponding formyl amides, which attract interest as polyfunctional intermediate products in organic synthesis. β-Keto amides are used in the synthesis of natural antibiotics [14]. Terminal propynamides are used as starting materials in the synthesis of various heterocyclic compounds possessing a broad spectrum of biological activity [15].

Known methods for the synthesis of terminal propynamides are based on acylation of amines with propynoic acid esters [16, 17], chloride [18], and anhydride [19] or propynoic acid itself in the presence of *N*,*N*′-dicyclohexylcarbodiimide [20]. A common disadvantage of the above procedures is the use of highly toxic and flammable (inflammation temperature 58°C) propynoic acid which also acts as skin irritant [21]. Moreover, the presence in propynoic acid esters of an additional electrophilic center, activated triple bond, favors formation of aminopropenoates [16, 22, 23].

To conclude, we have developed a simple and highly efficient procedure for the synthesis of terminal propynamides from accessible 3-trimethylsilylprop-2-ynamides [22, 24] using a catalytic amount of KF–Al_2O_3. Conditions have been found for selective one-step preparation of new mono- and dialkoxy amides as polyfunctional intermediate products for organic synthesis.

EXPERIMENTAL

The IR spectra were recorded on a Bruker IFS-25 spectrometer. The ^1H and ^{13}C NMR spectra were measured on a Bruker DPX-400 instrument relative to hexamethyldisiloxane as internal reference. Microwave-assisted reactions were performed in a 25-ml Teflon high-pressure reactor using an unmodified LG MS-1904H microwave furnace (700 W). Initial 3-trimethylsilylprop-2-ynamides were synthesized according to the procedure reported in [24]; KF–Al_2O_3 (KF concentration 40%) was prepared as described in [25].

Prop-2-ynamide (IIa). A mixture of 100 mg (0.71 mmol) of amide **Ia**, 5.1 mg (5 mol %) of KF–Al_2O_3, and 5 ml of methanol was stirred for 20 min at room temperature. The mixture was then evaporated under reduced pressure, and the residue was washed with chloroform and dried. Yield 40 mg (82%), mp 59–61°C [26]. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.88 s (1H, HC≡), 6.02 br.s and 5.88 br.s (1H each, NH_2).

***N*-Alkyl(aryl)prop-2-ynamides IIb–IIg (*general procedure*).** A mixture of 0.47 mmol of amide **Ib–Ig**, 3.4 mg (5 mol %) of KF–Al_2O_3, and 5 ml of methanol was stirred for 20 min at room temperature. The mixture was then treated with 1 ml of 5% hydrochloric acid and extracted with diethyl ether (in the synthesis of **IIb–IId**) or chloroform (**IIe–IIg**), and the extract was dried over $MgSO_4$ and evaporated under reduced pressure. The residue was propynamide **IIb–IIg** which required no additional purification.

***N*-Phenylprop-2-ynamide (IIb).** Yield 99%, mp 80–81°C [17]. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.92 s (1H, HC≡), 7.16 t (1H, 4-H, J = 7.60 Hz), 7.34 t (2H, *m*-H, J = 7.56 Hz), 7.54 d (2H, *o*-H, J = 7.52 Hz), 7.92 br.s (1H, NH).

***N*-Benzylprop-2-ynamide (IIc).** Yield 93%, mp 88–90°C [23]. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.80 s (1H, HC≡), 4.50 d (2H, C**H**$_2$Ph, J = 5.88 Hz), 6.12 br.s (1H, NH), 7.31 m (5H, Ph).

***N*-(2,5-Dichlorophenyl)prop-2-ynamide (IId).** Yield 99%, mp 112–113°C [18]. IR spectrum (KBr), ν, cm^{-1}: 3224 (NH, H–C≡), 2109 (C≡C), 1668 (C=O), 1587 (C=C_{arom}), 1522 (C–N, δNH). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 3.00 s (1H, HC≡), 7.07 m (1H, 4-H, J = 8.56 Hz), 7.31 d (1H, 3-H, J = 8.60 Hz), 8.46 s (1H, 6-H), 7.90 br.s (1H, NH). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 75.00 (≡C–), 77.41 (HC≡), 120.38 (C^2), 121.86 (C^6), 125.46 (C^4), 129.78 (C^3), 134.04 (C^5), 134.87 (C^1), 149.08 (C=O). Found, %: C 50.09; H 2.50; Cl 33.26; N 7.03. $C_9H_5Cl_2NO$. Calculated, %: C 50.50; H 2.35; Cl 33.13; N 6.74.

***N*-(3-Bromophenyl)prop-2-ynamide (IIe).** Yield 90%, mp 124–125°C [18]. IR spectrum (KBr), ν, cm^{-1}: 3271 (H–C≡), 3239 (NH), 2109 (C≡C), 1649 (C=O), 1593 (C=C_{arom}), 1547 (C–N, δNH). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.93 s (1H, HC≡), 7.20 t (1H, 5-H, J = 7.92 Hz), 7.29 d (1H, 4-H, J = 9.04 Hz), 7.46 d (1H, 6-H, J = 7.60 Hz), 7.73 s (1H, 2-H), 7.46 br.s (1H, NH). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 76.89 (≡C), 77.90 (HC≡), 118.11 (C^3), 121.42 and 121.96 (C^2, C^6), 126.34 (C^4), 130.13 (C^5), 139.72 (C^1), 149.45 (C=O). Found, %: C 48.53; H 2.59; Br 36.02; N 6.38. C_9H_6BrNO. Calculated, %: C 48.25; H 2.70; Br 35.66; N 6.25.

***N*-(2-Hydroxy-1,1-dimethylethyl)prop-2-ynamide (IIf).** Yield 83%, mp 135–136°C. IR spectrum (KBr), ν, cm^{-1}: 3400 (OH), 3290 (H–C≡), 3210 (NH), 2120 (C≡C), 1650 (C=O), 1560 (C–N, δNH). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 3.80 s (1H, HC≡), 3.34 s (2H, CH_2O), 1.18 s (6H, CH_3), 4.69 br.s (1H, OH), 7.88 br.s (1H, NH). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 23.11 (CH_3), 55.32 (N–C), 66.78

(C–O), 73.71 (≡C), 78.98 (HC≡), 151.12 (C=O). Found, %: C 59.78; H 7.20; N 9.61. $C_7H_{11}NO_2$. Calculated, %: C 59.56; H 7.85; N 9.92.

1-Morpholinoprop-2-yn-1-one (IIg). Yield 95%, mp 70–72°C [16]. IR spectrum (KBr), ν, cm^{-1}: 3200 (H–C≡), 2096 (C≡C), 1630 (C=O). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 3.16 s (1H, HC≡), 3.68 m (4H, NCH_2), 3.74 m (4H, OCH_2). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 75.33 (≡C), 79.53 (HC≡), 42.01 and 47.28 (NCH_2), 66.44 and 66.86 (OCH_2), 151.70 (C=O). Found, %: C 60.01; H 6.50; N 10.05. $C_7H_9NO_2$. Calculated, %: C 60.42; H 6.52; N 10.07.

(*Z*,*E*)-3-Methoxy-1-morpholinoprop-2-en-1-one (III). *a*. A Teflon reactor was charged with a mixture of 60 mg (0.28 mmol) of amide **Ig**, 2.1 mg (5 mol %) of KF–Al_2O_3, and 5 ml of methanol, and the reactor was placed into a microwave furnace and irradiated at a power of 700 W over a period of 15 min (in 2–4-min pulses followed by cooling to room temperature). The mixture was filtered, and the filtrate was evaporated under reduced pressure. Yield 43 mg (88%), mp 53–55°C (from hexane). IR spectrum (KBr), ν, cm^{-1}: 1670 (C=O); 1630, 1610 (C=C). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 3.70 s (3H, CH_3O, *E*), 3.75 s (3H, CH_3O, *Z*), 4.94 d (1H, =CHCO, *J* = 7.08 Hz, *Z*), 5.56 d (1H, =CHCO, *J* = 11.72 Hz, *E*), 6.23 d (1H, OCH=, *J* = 7.20 Hz, *Z*), 7.61 d (1H, OCH=, *J* = 11.84 Hz, *E*), 3.45 m and 3.55 m (2H each, NCH_2), 3.66 m (4H, OCH_2); (*E*:*Z* = 1.0:2.0). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 42.39 and 47.63 (CH_2N), 67.51 (CH_2O), 61.83 and 58.50 (CH_3O), 95.04 and 98.5 (=**C**HCO), 153.96 and 163.45 (=CHO), 165.57 and 166.81 (C=O). Found, %: C 56.59; H 7.32; N 8.19. $C_8H_{13}NO_3$. Calculated, %: C 56.13; H 7.65; N 8.18.

b. A mixture of 60 mg (0.28 mmol) of amide **Ig**, 4.9 mg (12 mol %) of KF–Al_2O_3, 1 ml of methanol, and 9 ml of acetonitrile was heated for 2 h at 65°C. The mixture was filtered, and the filtrate was evaporated under reduced pressure to obtain 41 mg (84%) of compound **III** as a mixture of *E* and *Z* isomers at a ratio of 1.0:2.0, mp 53–55°C (from hexane).

***N*-Alkyl-3,3-dimethoxypropanamides IVa and IVb (*general procedure*).** A mixture of 0.47 mmol of amide **Ic** or **Ig**, 3.4 mg (5 mol %) of KF–Al_2O_3, and 5 ml of methanol was heated at 65°C for 3 (**Ig**) or 7 h (**Ic**). The mixture was evaporated under reduced pressure, the residue was extracted with hot hexane, and the extract was filtered and evaporated under reduced pressure.

***N*-Benzyl-3,3-dimethoxypropanamide (IVa).** Yield 90%, oily substance. IR spectrum (film), ν, cm^{-1}: 1640 (C=O), 1580 (C=C_{arom}), 1530 (C–N, δNH), 1110 (C–O). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.60 d (2H, CH_2CO, *J* = 5.36 Hz), 3.39 s (6H, CH_3O), 4.47 d (2H, C**H**$_2$Ph, *J* = 5.64 Hz), 4.72 t (1H, CH, *J* = 5.36 Hz), 7.30 m (5H, Ph), 6.40 br.s (1H, NH). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 41.04 (**C**H_2CO), 43.47 (**C**H_2Ph), 54.20 (CH_3O), 102.23 (CH); 127.45, 127.58, 128.71, 136.85 (C_{arom}); 169.02 (C=O). Found, %: C 64.18; H 7.73; N 6.02. $C_{12}H_{17}NO_3$. Calculated, %: C 64.55; H 7.67; N 6.27.

3,3-Dimethoxy-1-morpholinopropan-1-one (IVb). Yield 83%, oily substance. IR spectrum (film), ν, cm^{-1}: 1630 (C=O), 1100 (C–O). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.68 d (2H, CH_2CO, *J* = 5.48 Hz), 3.43 s (6H, CH_3O), 3.52 m (4H, NCH_2), 3.72 m (4H, OCH_2), 4.70 t (1H, CH, *J* = 5.52 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 37.76 (**C**H_2CO), 42.14 and 46.61 (CH_2N), 66.98 (CH_2O), 54.89 (CH_3O), 103.51 (CH), 168.18 (C=O). Found, %: C 53.56; H 8.33; N 6.94. $C_9H_{17}NO_4$. Calculated, %: C 53.19; H 8.43; N 6.89.

REFERENCES

1. Clive, D.L.J., Bo, Y., Tao, Y., Daigneault, S., Wu, Y-J., and Meignan, G., *J. Am. Chem. Soc*., 1998, vol. 120, p. 10332; Thominet, O., Baker, J.R., Britton, H., Etheridge, Z.C., Soscia, M.G., and Caddick, S., *Org. Biomol. Chem*., 2007, vol. 5, p. 3703; Trost, B.M., Papillon, J.P.N., and Nussbaumer, T., *J. Am. Chem. Soc*., 2005, vol. 127, p. 17921; Yamamoto, Y., Yamashita, K., Hotta, T., Hashimoto, T., Kikuchi, M., and Nishiyama, H., *Chem. Asian J*., 2007, vol. 2, p. 1388.
2. Siemsen, P., Livingston, R.C., and Diederich, F., *Angew. Chem., Int. Ed*., 2000, vol. 39, p. 2632; Zhang, W. and Moore, J.S., *Angew. Chem., Int. Ed*., 2006, vol. 45, p. 4416.
3. Medvedeva, A.S., *Russ. J. Org. Chem*., 1996, vol. 32, p. 272.
4. Pierce, A.E., *Silylation of Organic Compounds. A Technique for Gas-Phase Analysis*, Rockford: Pierce Chemical, 1968, p. 3.
5. Coats, S.J., Link, J.S., Gauthier, D., and Hlasta, D.J., *Org. Lett*., 2005, vol. 7, p. 1469; Demina, M.M., Novopashin, P.S., Sarapulova, G.I., Larina, L.I., Smolin, A.S., Fundamenskii, V.S., Kashaev, A.A., and Medvedeva, A.S., *Russ. J. Org. Chem*., 2004, vol. 40, p. 1804; Bottaro, J.C., Schmitt, R.J., Bedford, C.D., Gilardi, R., and George, C., *J. Org. Chem*., 1990, vol. 55, p. 1916.
6. Nishinaga, T., Miyata, Y., Nodera, N., and Komatsu, K., *Tetrahedron*, 2004, vol. 60, p. 3375.

7. Casara, P., Danzin, C., Metcalf, B., and Jung, M., *J. Chem. Soc., Perkin Trans. 1*, 1985, p. 2201.
8. Shi Shun, A.L.K. and Tykwinski, R.R., *J. Org. Chem*., 2003, vol. 68, p. 6810.
9. De Meijere, A., Kozhushkov, S.I., Boese, R., Haumann, T., Yufit, D.S., Howard, J.A.K., Khaikin, L.S., and Trætteberg, M., *Eur. J. Org. Chem*., 2002, p. 485.
10. Kirkham, J.E.D., Courtney, T.D.L., Lee, V., and Baldwin, J.E., *Tetrahedron Lett*., 2004, vol. 45, p. 5645.
11. Tretyakov, E., Romanenko, G., Ikorskii, V., Stass, D., Vasiliev, V., Demina, M., Mareev, A., Medvedeva, A., and Ovcharenko, V., *Eur. J. Org. Chem*., 2007, p. 3639; Tretyakov, E., Tolstikov, S., Mareev, A., Medvedeva, A., Romanenko, G., Stass, D., Bogomyakov, A., and Ovcharenko, V., *Eur. J. Org. Chem*., 2009, p. 2548.
12. Kabalka, G.W., Wang, L., and Pagni, R.M., *Arkivoc*, 2001, part (iv), p. 5.
13. Albert, A. and Serjeant, E., *Ionization Constants of Acids and Bases*, London: Methuen, 1962. Translated under the title *Konstanty ionizatsii kislot i osnovanii*, Moscow: Khimiya, 1964, p. 131.
14. Iida, T., Hori, K., Nomura, K., and Yoshii, E., *Heterocycles*, 1994, vol. 38, p. 1839; Boeckman, R.K., Jr., Starrett, J.E., Jr., Nickell, D.G., and Sum, P.-E., *J. Am. Chem. Soc*., 1986, vol. 108, p. 5549.
15. Coppola, G. and Damon, R., *J. Heterocycl. Chem*., 1995, vol. 32, p. 1141; Pinto, A., Neuville, L., and Zhu, J., *Angew. Chem., Int. Ed*., 2007, vol. 46, p. 3291; Takao, K., Hayakawa, N., Yamada, R., Yamaguchi, T., Saegusa, H., Uchida, M., Samejima, S., and Tadano, K., *J. Org. Chem*., 2009, vol. 74, p. 6452.
16. Kanner, C. and Pandit, U., *Tetrahedron*, 1982, vol. 38, p. 3597.
17. Sánchez, V., Rebolledo, F., and Gotor, V., *Synlett*, 1994, p. 529.
18. Miller, L., US Patent no. 3210420, 1965; *Chem. Abstr*., 1965, vol. 63, p. 17971h.
19. Undheim, K. and Riege, L., *J. Chem. Soc., Perkin Trans. 1*, 1975, p. 1493.
20. Duckworth, D., Lee-Wong, S., Slawin, A., Smith, E., and Williams, D., *J. Chem. Soc., Perkin Trans. 1*, 1996, p. 815.
21. Raphael, R.A., *Acetylenic Compounds in Organic Synthesis*, New York: Academic, 1955.
22. Safronova, L.P., Medvedeva, A.S., and Vyazankin, N.S., *Zh. Obshch. Khim*., 1983, vol. 53, p. 1313.
23. Coppola, G. and Damon, R., *Synth. Commun*., 1993, vol. 23, p. 2003.
24. Medvedeva, A.S., Andreev, M.V., and Safronova, L.P., *Russ. J. Org. Chem*., 2010, vol. 46, p. 1466.
25. Yadav, V., Babu, K., and Mittal, M., *Tetrahedron*, 2001, vol. 57, p. 7047.
26. Ferris, T., Lee, P., and Farrar, T., *Magn. Reson. Chem*., 1997, vol. 35, p. 571.