Available online at www.sciencedirect.com
ScienceDirect
Mendeleev Commun., 2017, **27**, 175–177
Mendeleev Communications

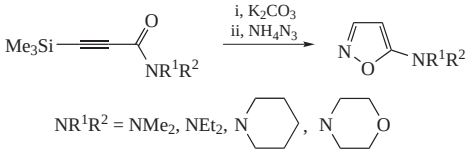
Synthesis of 5-aminoisoxazoles from 3-trimethylsilylprop-2-ynamides

Mikhail V. Andreev, Alevtina S. Medvedeva,* Lyudmila I. Larina and Maria M. Demina

A. E. Favorsky Irkutsk Institute of Chemistry, Siberian Branch of the Russian Academy of Sciences, 664033 Irkutsk, Russian Federation. Fax: +7 3952 419 346; e-mail: amedved@irioch.irk.ru

DOI: 10.1016/j.mencom.2017.03.023

Reaction between N,N-disubstituted 3-trimethylsilylprop-2-ynamides and ammonium azide under mild conditions affords hitherto unknown 5-aminoisoxazole derivatives in good yields.

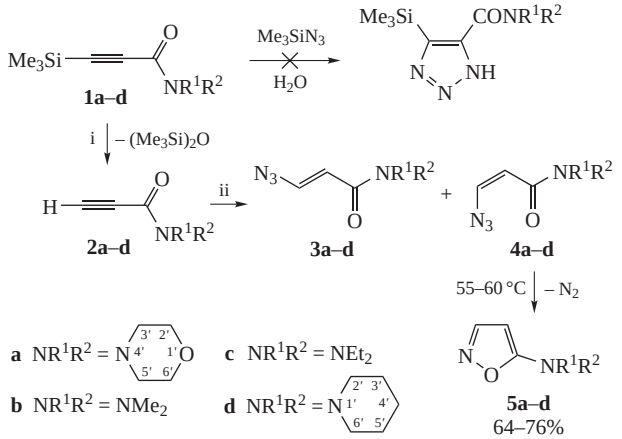


Isoxazoles are bioactive natural products, which are extensively used in pharmaceutical industry[1] and are employed as versatile building blocks in the synthesis of new biologically potent molecules.[2] New strategy for the design of hybrid molecular systems which combine several pharmacophores, including 1,2-isoxazole fragment, on the same scaffold, is a well-established pharmacology-oriented approach to the synthesis of new drugs.[3] 5-Aminoisoxazoles exhibiting various biological activities[4] generate great interest. N-Unsubstituted 5-aminoisoxazoles are precursors for the synthesis of 3-, 4- and N-functionalized derivatives and isoxazole fused heterocycles.[5]

The common routes for the preparation of 5-N-unsubstituted aminoisoxazoles involve the addition of hydroxylamine to functionalized nitriles,[4(c),5(b),6] cyanation of *N*,*N*-bis(siloxy)enamines with Me_3SiCN.[7] *N*,*N*-Dialkyl-5-aminoisoxazoles were obtained by 1,3-dipolar cycloaddition of nitrile oxides to 2-(dialkylamino)-acrylonitriles[8] or substituted ynamines.[9]

The present paper describes a novel metal-free synthesis of hitherto unknown 3,4-unsubstituted 5-*N*,*N*-dialkylaminoisoxazoles from available 3-trimethylsilylprop-2-ynamides[10] and ammonium azide.

Recently, we have shown the efficacy of water as a solvent for efficient metal-free synthesis of 1,2,3-triazolecarbaldehydes from propynals and trimethylsilyl or benzyl azide[11] as compared to thermal Huisgen processes,[12] and in preparation of 5-R-4-alkenyl-1*H*-1,2,3-triazoles *via* the three-component β-catalyzed reaction of the propynals, trimethylsilyl azide and malononitrile at room temperature.[13] However, the attempt to accomplish 1,3-dipolar cycloaddition of trimethylsilyl azide to 3-trimethylsilylprop-2-ynoic acid morpholide **1a** under analogous conditions failed. Instead, only the starting amide **1a** was recovered from the reaction mixture.



Scheme 1 *Reagents and conditions*: i, K_2CO_3 (10 mol%), H_2O, room temperature; ii, NH_4N_3 or Me_3SiN_3, H_2O, room temperature.

The reaction between terminal propynamide **2a**, generated *in situ* by desilylation of compound **1a** with K_2CO_3 (10 mol%), and trimethylsilyl azide in water at room temperature for 16 h unexpectedly afforded a mixture of (*Z*)-enazide **4a**, (*E*)-enazide **3a**, 5-aminoisoxazole **5a** along with **2a** in a molar ratio of 53:2:4:41, respectively (^{1}H NMR monitoring) (Scheme 1, Table 1).† The variation of the starting azide nature, time, temperature and a ratio of reactants on the model reaction of amide **1a** allowed us to optimize conditions for the synthesis of desired isoxazole **5a** in 70% isolated yield (Table 1, entry 6).

The use of 5-fold excess of more available ammonium azide, generation of the intermediate (*Z*)-enazides **4a**–**d** at room tem-

† The ^{1}H, ^{13}C and ^{15}N NMR spectra were recorded at room temperature on Bruker DPX-400 and Bruker AV-400 spectrometers (400.13, 100.61 and 40.56 MHz, respectively) in $CDCl_3$ solution with accuracy of 0.01, 0.02 and 0.1 ppm, respectively, and referred to TMS (^{1}H, ^{13}C) and nitromethane (^{15}N). The values of the $\delta_{^{15}N}$ were obtained through the 2D ^{1}H–^{15}N HMBC experiment. IR spectra were measured on a Bruker IFS-25 spectrometer. Elemental analyses were carried out on a Flash EA 1112 Series CHNS-O analyzer. Melting points were determined on a Kofler apparatus and were not corrected. The completion of the reaction was monitored by ^{1}H NMR. Column chromatography was performed on silica gel [Alfa Aesar, 0.06–0.20 mm (70–230 mesh)] with chloroform–methanol (100 : 2) as an eluent.

Reaction between **1a** *and* Me_3SiN_3. A mixture of *N*-[3-(trimethylsilyl)-2-propynoyl]morpholine **1a** (100 mg, 0.47 mmol) and K_2CO_3 (6 mg, 10 mol%) in H_2O (1.5 ml) was stirred for 1.5 h at room temperature and trimethylsilyl azide (60 mg, 0.52 mmol) was added. The mixture was stirred at room temperature and small aliquots (0.5 ml) from the reaction mixture were extracted with $CDCl_3$ (2×0.7 ml) after 16 or 40 h and analyzed by ^{1}H NMR spectroscopy. After 40 h along with *N*-(prop-2-ynoyl)-morpholine **2a**,[19] azidovinyl amides **3a**, **4a** and target aminoisoxazole **5a** were detected in a molar ratio of 9 : 4 : 65 : 22, respectively. According to ^{1}H NMR data, azido alkanes **3a** and **4a** are stereoisomers (4 : 65). ^{1}H NMR, δ: 3.47 (br.m, 2H, NCH_2), 3.65 (br.m, 6H, NCH_2, OCH_2), 5.38 (d, 1H, =CHCO, ^3J 8.6 Hz, *Z*-isomer), 5.99 (d, 1H, =CHCO, ^3J 12.7 Hz, *E*-isomer), 6.46 (d, 1H, N_3CH=, ^3J 8.6 Hz, *Z*-isomer), 7.36 (d, 1H, N_3CH=, ^3J 12.7 Hz, *E*-isomer).

Table 1 Optimization of the synthesis of 4-(5-isoxazolyl)morpholine **5a** from **1a**.

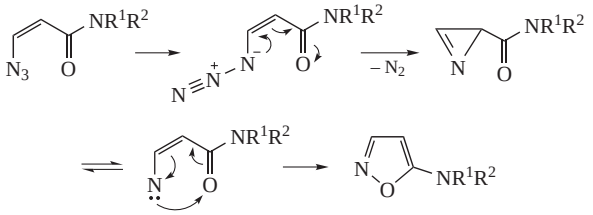
Entry	Azide (equiv.)	Reaction conditions	Product ratio (^{1}H NMR)				Isolated yield of **5a** (%)
			2a	**3a**	**4a**	**5a**	
1	Me_3SiN_3 (1)	25 °C, 16 h	41	2	53	4	–
2	Me_3SiN_3 (1)	25 °C, 40 h	9	4	65	22	–
3	NH_4N_3 (1)	25 °C, 16 h	11	1	76	12	–
4	NH_4N_3 (1)	25 °C, 40 h	1	4	64	31	–
5	NH_4N_3 (5)	25 °C, 4 h	–	1	96	3	–
6[a]	NH_4N_3 (5)	25 °C, 4 h; then 55 °C, 2 h	–	2	–	98	70[b]
7	NH_4N_3 (1)	MW, 80 °C, 80 min	–	4	–	96	49[c]

[a] Extraction with CH_2Cl_2, removal of the solvent followed by heating of the residue at 55–60 °C for 2 h. [b] Vacuum distillation. [c] Column chromatography.

perature in water followed by extraction with CH_2Cl_2, and final heating at 55–60 °C provided the selective multigram synthesis of 5-aminoisoxazoles **5a**–**d** in good yields (64–76%) after vacuum distillation.‡

Microwave (MW) irradiation can also be successfully employed to prepare 4-(5-isoxazolyl)morpholine **5a** from *in situ* generated propynamide **2a** in water. The MW-assisted reaction with ammonium azide in equimolar ratio (80 °C, 80 min) gave the target isoxazole **5a** in 49% isolated yield (see Table 1, entry 7).§

A plausible mechanism for the conversion of (*Z*)-vinylazides, bearing a conjugative amide group, involves generation of highly strained three-membered 2*H*-azirines *via* the loss of dinitrogen, cleavage of the C–N bond, formation of intermediate vinyl nitrenes and intramolecular cyclization into 5-aminoisoxazoles with participation of the amide carbonyl moiety (Scheme 2).



Scheme 2

The intermediate 2*H*-azirines were never detected by us in the reaction mixture. The formation of 2*H*-azirines under thermolysis of β-aldehyde, ketone, or ester-substituted vinyl azides to afford isoxazoles is known.[14] However, the conversion of carboxamide vinyl azides into the corresponding 5-aminoisoxazoles has not been reported until now. It is pertinent to note that the ^{1}H NMR monitoring confirms the dominant formation of the *Z*-isomer of intermediate β-azido enamides **4a**–**d**. The content of the minor *E*-isomer **3a**–**d** in the reaction mixture does not exceed 5%. Note that tandem transformation of trimethylsilylpropynamides into 3-aminoprop-2-enamides by the action of primary amines in MeOH gave also the corresponding *Z*-isomers as major products.[15]

The reactivity of azide ion in conjugate addition to the triple bond of *in situ* generated propynamides **2a**–**d** to form the intermediate azido alkenes substantially depends on the nature of amide moiety. The ^{1}H NMR monitoring evidences that duration of the key intermediate *Z*-isomer formation varies from 4 to 40 h in the series: $N(CH_2CH_2)_2O$ (**a**) < NMe_2 (**b**) < $N(CH_2CH_2)_2CH_2$ (**d**) < < NEt_2 (**c**) in accordance with the increase of electron-donating properties of amines.[16]

Target compounds **5a**–**d** are well soluble in water and polar organic solvents. Their structure was confirmed by IR and ^{1}H, ^{13}C NMR technique and elemental analyses. Their 2D ^{15}N NMR HMBC {^{1}H–^{15}N} ($CDCl_3$) spectra contain cross-peaks of N-2 atom with H-3 and H-4 protons of the isoxazole cycle at –20.0 to –26.6 ppm and cross-peaks of the amino group nitrogen with protons of neighboring *N*,*N*-dialkyl substituents at –300.8 to –329.2 ppm.

‡ 3-Trimethylsilylprop-2-ynamides **1a**–**d** were prepared by published procedure.[12]

Compounds **5a**–**d** *(general procedure).* A mixture of 3-trimetylsilylprop-2-ynamide **1** (19 mmol) and K_2CO_3 (240 mg, 10 mol%) in H_2O (20 ml) was stirred for 1.5 h at room temperature, and then solution of NaN_3 (6.2 g, 95 mmol) and NH_4Cl (5.1 g, 95 mmol) in H_2O (40 ml) was added. The mixture was stirred for 4–40 h at room temperature and extracted with CH_2Cl_2 (2×40 ml). The extract was dried over Na_2SO_4, and the solvent was removed by distillation at atmospheric pressure using water bath at 65–70 °C followed by heating of the residue at this temperature until the nitrogen bubbles evolution stopped (*ca.* 2 h). The oil residue was distilled *in vacuo*.

4-(5-Isoxazolyl)morpholine **5a** was prepared for 6 h in 70% yield (2.05 g), white solid, mp 30–31 °C, bp 111–114 °C (4 mbar). ^{1}H NMR, δ: 3.25 (t, 4H, H-3′, H-5′, ^3J 4.9 Hz), 3.72 (t, 4H, H-2′, H-6′, ^3J 4.9 Hz), 4.95 (d, 1H, H-4, ^3J 1.9 Hz), 7.93 (d, 1H, H-3, ^3J 1.9 Hz). ^{13}C NMR, δ: 46.58 (C-3′, C-5′, $^1J_{CH}$ 138.5 Hz), 65.72 (C-2′, C-6′, $^1J_{CH}$ 144.1 Hz), 77.68 (C-4, $^1J_{CH}$ 182.1 Hz, $^2J_{CH}$ 9.2 Hz), 151.71 (C-3, $^1J_{CH}$ 182.1 Hz, $^2J_{CH}$ 5.2 Hz), 170.52 (C-5). ^{15}N NMR, δ: –313.9 (NCH_2), –20.0 (N-2, $^2J_{NH}$ 15.7 Hz). IR (KBr, ν/cm^{-1}): 727, 898, 911, 993, 1072, 1118, 1246, 1269, 1328, 1461, 1504, 1598, 1662, 2858, 2969, 3084, 3110, 3145. Found (%): C, 54.54; H, 6.52; N, 18.50. Calc. for $C_7H_{10}N_2O_2$ (%): C, 54.54; H, 6.54; N, 18.17.

N,N-*Dimethyl-5-isoxazolamine* **5b** was prepared for 16 h in 76% yield (1.62 g), viscous white liquid, bp 86–89 °C (17 mbar), n_D^{20} = 1.4960. ^{1}H NMR, δ: 2.89 (s, 6H, Me), 4.77 (d, 1H, H-4, ^3J 2.0 Hz), 7.86 (d, 1H, H-3, ^3J 2.0 Hz). ^{13}C NMR, δ: 38.46 (Me, $^1J_{CH}$ 137.7 Hz, $^3J_{CH}$ 3.6 Hz), 75.82 (C-4, $^1J_{CH}$ 180.9 Hz, $^2J_{CH}$ 9.5 Hz), 151.86 (C-3, $^1J_{CH}$ 180.9 Hz, $^2J_{CH}$ 5.3 Hz), 170.73 (C-5). ^{15}N NMR, δ: –329.2 (NMe), –24.1 (N-2, $^2J_{NH}$ 14.3 Hz). IR (microlayer, ν/cm^{-1}): 707, 916, 1001, 1052, 1143, 1240, 1360, 1430, 1519, 1619, 2811, 2923, 3097, 3150. Found (%): C, 53.37; H, 6.91; N, 24.77. Calc. for $C_5H_8N_2O$ (%): C, 53.56; H, 7.19; N, 24.98.

N,N-*Diethyl-5-isoxazolamine* **5c** was prepared for 42 h in 71% yield (1.89 g), viscous white liquid, bp 78–79 °C (3 mbar), n_D^{20} = 1.4903. ^{1}H NMR, δ: 1.19 (t, 6H, Me, ^3J 7.2 Hz), 3.35 (q, 4H, CH_2, ^3J 7.2 Hz), 4.80 (d, 1H, H-4, ^3J 2.0 Hz), 7.94 (d, 1H, H-3, ^3J 2.0 Hz). ^{13}C NMR, δ: 13.10 (Me, $^1J_{CH}$ 127.2 Hz), 43.95 (CH_2, $^1J_{CH}$ 136.7 Hz, $^2J_{CH}$ 4.1 Hz), 75.11 (C-4, $^1J_{CH}$ 181.3 Hz, $^2J_{CH}$ 9.6 Hz), 152.10 (C-3, $^1J_{CH}$ 181.3 Hz, $^2J_{CH}$ 5.5 Hz), 169.62 (C-5). ^{15}N NMR, δ: –300.8 (NEt), –26.6 (N-2, $^2J_{NH}$ 15.3 Hz). IR (microlayer, ν/cm^{-1}): 704, 786, 910, 1027, 1054, 1080, 1097, 1181, 1217, 1273, 1362, 1380, 1450, 1518, 1603, 2876, 2936, 2976, 3092, 3149. Found (%): C, 60.13; H, 8.82; N, 20.00. Calc. for $C_7H_{12}N_2O$ (%): C, 59.98; H, 8.63; N, 19.98.

1-(5-Isoxazolyl)piperidine **5d** was prepared for 30 h in 64% yield (1.85 g), white solid, mp 28–29 °C, bp 101–102 °C (4 mbar). ^{1}H NMR, δ: 1.59–1.69 (m, 6H, H-3′, H-4′, H-5′), 3.28 (t, 4H, H-2′, H-6′, ^3J 5.6 Hz), 4.93 (d, 1H, H-4, ^3J 2.0 Hz), 7.98 (d, 1H, H-3, ^3J 2.0 Hz). ^{13}C NMR, δ: 23.81 (C-4′, $^1J_{CH}$ 128.6 Hz, $^2J_{CH}$ 4.9 Hz), 24.81 (C-3′, C-5′, $^1J_{CH}$ 128.6 Hz, $^2J_{CH}$ 3.4 Hz), 47.71 (C-2′, C-6′, $^1J_{CH}$ 136.8 Hz, $^2J_{CH}$ 2.8 Hz), 76.78 (C-4, $^1J_{CH}$ 181.3 Hz, $^2J_{CH}$ 9.4 Hz), 151.91 (C-3, $^1J_{CH}$ 181.3 Hz, $^2J_{CH}$ 5.4 Hz), 170.89 (C-5). ^{15}N NMR, δ: –306.8 (NCH_2), –25.3 (N-2, $^2J_{NH}$ 15.2 Hz). IR (KBr, ν/cm^{-1}): 717, 759, 892, 909, 985, 1029, 1064, 1136, 1193, 1225, 1255, 1327, 1355, 1389, 1452, 1505, 1598, 2855, 2939, 3081, 3102, 3137. Found (%): C, 63.28; H, 7.90; N, 18.13. Calc. for $C_8H_{12}N_2O$ (%): C, 63.13; H, 7.95; N, 18.41.

§ *MW-assisted synthesis of* **5a**. A mixture of **1a** (400 mg, 1.88 mmol) and K_2CO_3 (24 mg, 10 mol%) in H_2O (2.0 ml) was stirred in a sealed 10 ml Pyrex vial at room temperature for 1 h, then solution of NaN_3 (124 mg, 1.88 mmol) and NH_4Cl (100 mg, 1.88 mmol) in H_2O (4.0 ml) was added. The vial was placed in the cavity of an Anton Paar Monowave 300 reactor and irradiated for 80 min at 80 °C. After cooling to room temperature, the mixture was extracted with CH_2Cl_2 (2×4 ml) and the extract was dried over Na_2SO_4. The solvent was evaporated *in vacuo*, and column chromatography of the residue afforded the target compound **5a**, white solid, mp 30–31 °C, yield 142 mg (49%).

We have recently elaborated an efficient one-pot synthesis of 3-trimethylsilylprop-2-ynamides from accessible and environmentally benign trimethylsilylpropynoic acid.[10] It should be noted that application of 3-trimethylsilylprop-2-ynamides as the starting substrates in the synthesis of the target 5-aminoisoxazoles is more advantageous as compared to terminal propynamides. Known methods for the preparation of terminal propynamides[17] are based on the use of highly toxic, flammable (inflammation temperature 58 °C) and skin-irritating propynoic acid.[18] Highly efficient procedure for the synthesis of terminal propynamides from trimethylsilylated analogues catalyzed by $KF–Al_2O_3$ has been reported earlier.[19]

In summary, we have implemented a novel facile metal-free selective synthesis of so far unknown N,N-substituted 5-aminoisoxazoles using available amides of 3-(trimethylsilyl)propynoic acid and ammonium azide under mild conditions. It has been shown for the first time that successive conversion of generated in water (*Z*)-azidovinylamides as key intermediates into 5-aminoisoxazoles occurs with the involvement of the CO moiety of the amide group. New 3,4-unsubstituted 5-*N*,*N*-dialkylisoxazolamines are potential biologically active substances, polydentate ligands, and reagents for synthesis of new heterocyclic compounds.

An alternative approach to the synthesis of these 5-aminoisoxazoles *via* the cycloaddition of nitrile oxides to terminal ynamines[9,20] is difficult to implement because of instability of unsubstituted nitrile oxide (fulminic acid)[21] and less accessibility of ynamines[22] in comparison with trimethylsilylpropynamides.

The main results were obtained using the equipment of Baikal Analytical Center of Collective Use SB RAS.

References

1 (*a*) J. B. Sperry and D. L. Wright, *Curr. Opin. Drug Discov. Dev*., 2005, **8**, 723; (*b*) J. P. Waldo and R. C. Larock, *J. Org. Chem.*, 2007, **72**, 9643; (*c*) K. A. Kumar and P. Jayaroopa, *Int. J. Pharm. Chem. Biol. Sci*., 2013, **3**, 294.

2 (*a*) S. Grecian and V. V. Fokin, *Angew. Chem. Int. Ed.*, 2008, **47**, 8285; (*b*) V. P. Kislyi, E. B. Danilova and V. V. Semenov, *Mendeleev Commun*., 2012, **22**, 85; (*c*) A. V. Galenko, A. F. Khlebnikov, M. S. Novikov, V. V. Pakalnis and N. V. Rostovskii, *Russ. Chem. Rev.*, 2015, **84**, 335; (*d*) F. Hu and M. Szostak, *Adv. Synth. Catal*., 2015, **357**, 2583.

3 (*a*) S. G. Zlotin, A. M. Churakov, O. A. Luk'yanov, N. N. Makhova, A. Yu. Sukhorukov and V. A. Tartakovsky, *Mendeleev Commun*., 2015, **25**, 399; (*b*) V. P. Ananikov, K. I. Galkin, M. P. Egorov, A. M. Sakharov, S. G. Zlotin, E. A. Redina, V. I. Isaeva, L. M. Kustov, M. L. Gening and N. E. Nifantiev, *Mendeleev Commun*., 2016, **26**, 365; (*c*) A. N. Vereshchagin, M. N. Elinson, Yu. E. Anisina, F. V. Ryzhkov, A. S. Goloveshkin, I. S. Bushmarinov, S. G. Zlotin and M. P. Egorov, *Mendeleev Commun.*, 2015, **25**, 424.

4 (*a*) R. G. Micetich, R. Raap and C. G. Chin, *J. Med. Chem.*, 1971, **14**, 856; (*b*) K. Tomita, Y. Tsuzuki, K. Shibamori, M. Tashima, F. Kajikawa, Y. Sato, S. Kashimoto, K. Chiba and K. Hino, *J. Med. Chem*., 2002, **45**, 5564; (*c*) M. Mączyński, S. Ryng, J. Artym, M. Kocieba, M. Zimecki, K. Brudnik and J. T. Jodkowski, *Acta Pol. Pharm.*, 2014, **71**, 71.

5 (*a*) W. S. Hamama, M. E. Ibrahim and H. H. Zoorob, *Synth. Commun*., 2013, **43**, 2393; (*b*) A. Davoodnia, M. Bakavoli, N. Pooryaghoobi and M. Roshani, *Heterocycl. Commun*., 2007, **13**, 323; (*c*) G. J. Yu, B. Yang, A. S. Verkman and M. J. Kurth, *Synlett*, 2010, 1063; (*d*) S. B. Alyabiev, D. V. Kravchenko and A. V. Ivachtchenko, *Mendeleev Commun.*, 2008, **18**, 144; (*e*) E. A. Muravyova, V. V. Tkachenko, S. M. Desenko, Y. V. Sen'ko, T. J. J. Müller, E. V. Vashchenko and V. A. Chebanov, *Arkivoc*, 2013, **iii**, 338.

6 (*a*) L. Johnson, J. Powers, F. Ma, K. Jendza, B. Wang, E. Meredith and N. Mainolfi, *Synthesis*, 2013, **45**, 171; (*b*) J. Khalafy, K. Akbari Dilmaghani, L. Soltani and A. Poursattar-Marjani, *Chem. Heterocycl. Compd*., 2008, **44**, 729 (*Khim. Geterotsikl. Soedin.*, 2008, 907); (*c*) L. N. Sobenina, V. N. Drichkov, A. I. Mikhaleva, O. V. Petrova, I. A. Ushakov and B. A. Trofimov, *Tetrahedron*, 2005, **61**, 4841.

7 A. V. Lesiv, S. L. Ioffe, Yu. A. Strelenko, I. V. Bliznets and V. A. Tartakovsky, *Mendeleev Commun.*, 2002, 99.

8 A. Saad, M. Vaultier and A. Derdour, *Molecules*, 2004, **9**, 527.

9 G. Himbert, H. Kuhn and M. Barz, *Liebigs Ann. Chem*., 1990, 403.

10 A. S. Medvedeva, M. V. Andreev and L. P. Safronova, *Russ. J. Org. Chem*., 2010, **46**, 1466 (*Zh. Org. Khim.*, 2010, **46**, 1463).

11 (*a*) M. M. Demina, T. L. H. Nguyen, N. S. Shaglaeva, A. V. Mareev and A. S. Medvedeva, *Russ. J. Org. Chem*., 2012, **48**, 1582 (*Zh. Org. Khim*., 2012, **48**, 1611); (*b*) A. S. Medvedeva, M. M. Demina, T. L. H. Nguyen, T. D. Vu, D. A. Bulanov and V. V. Novokshonov, *Russ. J. Org. Chem.*, 2013, **49**, 1221 (*Zh. Org. Khim.*, 2013, **49**, 1236).

12 M. M. Demina, P. S. Novopashin, G. I. Sarapulova, L. I. Larina, A. S. Smolin, V. S. Fundamenskii, A. A. Kashaev and A. S. Medvedeva, *Russ. J. Org. Chem.*, 2004, **40**, 1804 (*Zh. Org. Khim*., 2004, **40**, 1852).

13 A. S. Medvedeva, M. M. Demina, T. D. Vu, M. V. Andreev, N. S. Shaglaeva and L. I. Larina, *Mendeleev Commun*., 2016, **26**, 326.

14 (*a*) T. M. V. D. Pinho e Melo, C. S. J. Lopes, A. M. d'A. Rocha Gonsalves and R. C. Storr, *Synthesis*, 2002, 605; (*b*) K. Banert, in *Organic Azides: Syntheses and Applications*, eds. S. Bräse and K. Banert, John Wiley & Sons, Chichester, 2010, part 2, p. 115.

15 M. V. Andreev, A. S. Medvedeva and L. P. Safronova, *Russ. J. Org. Chem*., 2013, **49**, 822 (*Zh. Org. Khim*., 2013, **49**, 839).

16 *Tablitsy konstant skorostei i ravnovesiya geteroliticheskikh organicheskikh reaktsii (Tables of Rate and Equilibrium Constants of Heterolytic Organic Reactions)*, ed. V. A. Palm, VINITI, Moscow, 1976, vol. 2 (1) (in Russian).

17 (*a*) G. M. Coppola and R. E. Damon, *Synth. Commun.*, 1993, **23**, 2003; (*b*) K. Undheim and L. A. Riege, *J. Chem. Soc., Perkin Trans. 1*, 1975, 1493.

18 R. A. Raphael, *Acetylenic Compounds in Organic Synthesis*, Academic Press, New York, 1955.

19 M. V. Andreev, L. P. Safronova and A. S. Medvedeva, *Russ. J. Org. Chem*., 2011, **47**, 1797 (*Zh. Org. Khim*., 2011, **47**, 1761).

20 H. Li, L. You, X. Zhang, W. L. Johnson, R. Figueroa and R. P. Hsung, *Heterocycles*, 2007, **74**, 553.

21 C. Grundmann, *Synthesis*, 1970, 344.

22 A. R. Katritzky, R. Jiang and S. K. Singh, *Heterocycles*, 2004, **63**, 1455.

Received: 4th August 2016; Com. 16/5017