Chemistry of Heterocyclic Compounds, Vol. 43, No. 7, 2007

THE MANNICH REACTION IN THE SYNTHESIS OF N,S-CONTAINING HETEROCYCLES 3*. UNEXPECTED DIRECTION OF THE AMINOMETHYLATION REACTION OF N-METHYLMORPHOLINIUM 1-AMINO-2,4-DICYANO-4-ETHOXYCARBONYL-1,3-BUTADIENETHIOLATE. ONE STAGE CASCADE SYNTHESIS OF NEW DERIVATIVES OF PYRIDO[1,2-*a*][1,3,5]TRIAZINE

V. V. Dotsenko[1], S. G. Krivokolysko[1], E. B. Rusanov[2], A. V. Gutov[2], and V. P. Litvinov[3]

The interaction of N-methylmorpholinium 1-amino-2,4-dicyano-4-ethoxycarbonyl-1,3-butadienethiolate with primary amines and formaldehyde leads to the formation of ethyl esters of 7-cyano-6-thioxo-1,3,4,6-2H-pyrido[1,2-a][1,3,5]triazine-9-carboxylic acid in place of the expected derivatives of pyrido[2,1-b][1,3,5]thiadiazine. The structure of the ethyl ester of 7-cyano-3-phenyl-6-thioxo-1,3,4,6-2H-pyrido[1,2-a][1,3,5]triazine-9-carboxylic acid was demonstrated by X-ray structural analysis.

Keywords: N-methylmorpholinium 1-amino-2,4-dicyano-4-ethoxycarbonyl-1,3-butadienethiolate, pyrido-[1,2-*a*][1,3,5]triazines, cascade heterocyclization, Mannich reaction, X-ray structural analysis.

It is known from numerous literature data that the three-component Mannich cyclocondensation of a series of mercaptoazoles and -azines, formaldehyde, and primary amines serves as a convenient method of obtaining various heterocyclic systems annelated with the 1,3,5-thiadiazine ring [2-11]. Recently heterocyclization of a similar type was used successfully by us to obtain derivatives of pyrido-[2,1-*b*][1,3,5]thiadiazine [12, 13]. Continuing investigations of polycomponent cascade reactions [14], we turned our attention to N-methylmorpholinium 1-amino-2,4-dicyano-4-ethoxycarbonyl-1,3-butadienethiolate (**1**) [15] as a promising subject for carrying out cascade heterocyclization under the conditions of the Mannich reaction. This diene is readily available and fairly stable. Even on boiling for 3 h it crystallizes out from

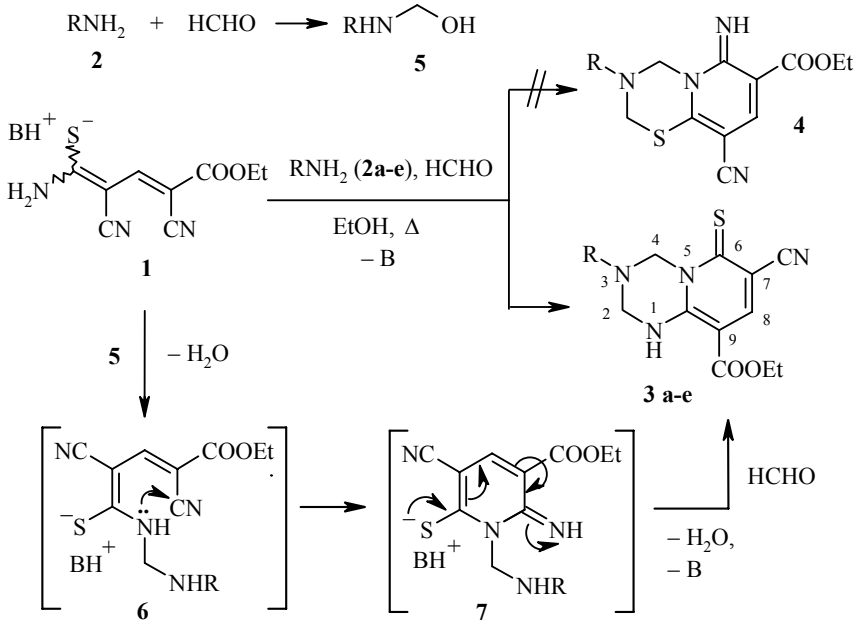
* For Part 2 see [1].

[1]ChemEx Laboratory, East-Ukrainian Vladimir Dal National University, Lugansk 91034, Ukraine; e-mail: ksg@lep.lg.ua. [2]Institute of Organic Chemistry, National Academy of Sciences of Ukraine; Kiev 02094; e-mail: iochkiev@ukrpack.net. [3]N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, Moscow 117913; e-mail: vpl@mail.ioc.ac.ru. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 7, pp. 1075-1081, July, 2007. Original article submitted April 3, 2006.

 0009-3122/07/4307-0906

alcoholic solution in unchanged form. Aspects of the spatial structure of compound **1** were not considered in [15], but it is entirely probable that its comparative stability towards cyclization is explained by the favorable *E,E*-configuration, as was shown previously [16, 17] in the example of other functionally substituted butadienes of similar type. In this connection it is of particular interest that on treatment with alkyl halides thiolate **1** is spontaneously cyclized with the formation of 6-alkylthio-2-amino-5-cyanonicotinic acid esters [15, 18]. Butadienethiolate **1** was therefore considered by us as a convenient alicyclic synthon permitting, under Mannich reaction conditions, one stage accomplishment of the cascade synthesis of bicyclic products, *viz*. derivatives of pyrido[2,1-*b*][1,3,5]thiadiazine.

However the experiment gave an unexpected result. It turned out that the interaction of compound **1** with primary amines **2** and an excess of formaldehyde in ethanol leads on brief heating to the formation of ethyl esters of 7-cyano-6-thioxo-1,3,4,6-2H-pyrido[1,2-*a*][1,3,5]triazine-9-carboxylic acid **3a-e** and not derivatives of pyrido[2,1-*b*][1,3,5]thiadiazine **4**.



B = N-methylmorpholine; **2, 3 a** R = Ph, **b** R = 3,4-$Me_2C_6H_3$,
c R = furfuryl, **d** R = 4-FC_6H_4, **e** R = 2-$EtOC_6H_4$

Presumably, in the first stage of the process butadienethiolate **1** under the action of N-(hydroxymethyl)amine **5**, formed as an intermediate, is converted into N-aminomethyl derivative **6**. This is in agreement with the data of [19], indicating the predominant aminomethylation of compounds with a thioamide fragment just at the nitrogen atom. Then intermediate **6**, existing in all appearances in the *s*-cissoid form, undergoes selective cyclization with the formation of pyridine **7**, which reacts with a second molecule of formaldehyde to form the 1,3,5-triazine ring in the bicyclic molecule **3**.

It is nessary to note that the number of methods of synthesizing derivatives of pyrido[1,2-*a*]-[1,3,5]triazine is limited [20-25]. However, compounds of this class are of practical interest being strong antagonists of the 5-hydroxytryptamine receptors 5-HT_2 and 5-HT_{2a} [26-28] and are active anthelmintic and fungicidal agents [28, 29]. These data, the availability of the starting materials, and the simplicity of carrying out the synthesis, in combination with the fairly high yields of the desired products (73-85%), indicate the promise of the method developed by us for obtaining pyridotriazines.

The structure of [1,2-*a*][1,3,5]triazines **3a-e** was confirmed by data of spectral investigations. In the IR spectra of the synthesized compounds absorption bands were detected for stretching vibrations in the ranges ν = 3175-3210, 2217-2230, and 1675-1690 cm^{-1}, indicating the presence of imino group, a conjugated nitrile function, and ester groups respectively. Of the number of the most characteristic signals observed in the ^{1}H NMR spectra of pyrido[1,2-*a*][1,3.5]triazines, it is necessary to mention the sharp singlet of the proton H-8 of the pyridine ring (δ = 7.95-8.03) and the broadened peak of the NH proton resonating in a narrow range (δ 9.93-9.96 ppm) for compounds **3a,b,d,e**, while in the case of compound **3c,** bearing a furfuryl substituent in position 3, the signal of the imino group was displaced somewhat towards higher field (δ = 9.74 ppm). The protons of the 1,3,5-triazine ring were detected in the region δ = 5.39-6.08 (H_2-4) and δ = 4.54-5.19 ppm (H_2-2) and are multiplets, which are resolved at 200 MHz as broadened peaks. It is necessary to note that since it is impossible to characterize the fine structure and coupling constants for clearly multiplet signals of NH and H_2-2, presumably due to the low values of the corresponding J_{NH-H} constant, the isomeric structures **3** and **4** are difficult to distinguish on the basis of data of IR and ^{1}H NMR spectra. We therefore investigated the structure of the compound with the proposed structure **3a** by the X-ray structural method.

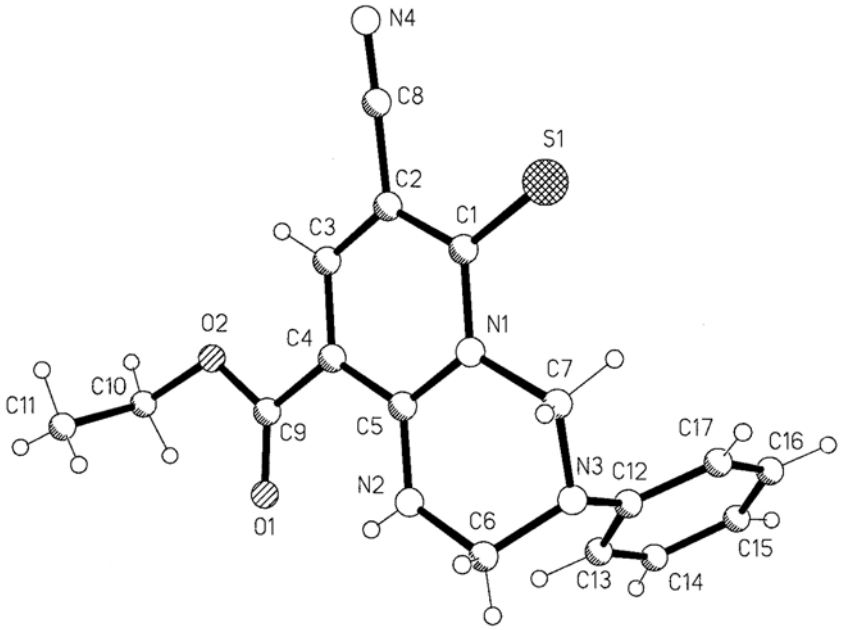


Fig. 1. General shape of the **3a** molecule.

In the compound **3a** molecule (Fig. 1) the central pyridine ring C(1-5)N(1) is somewhat distorted, the maximum deviation of an atom from the mean square plane is 0.047(1) Å. The bicyclic system N(1-3)C(1-7) is not planar, the mean square deviation is 0.181 Å. The N(1-3)C(5-7) heterocycle has an *envelope* conformation, N(1-2)C(5-7) atoms form a mean square plane with maximum deviation 0.043(1), but the C(6-7)N(3) atoms form with it a corner of 51.79(14)°. The dihedral angle between the N(1-2)C(5-7) fragment of the heterocycle and the N(1)C(1-5) pyridine ring is 7.16(1)°. The C=S bond length (1.677(2) Å) is within the limits characteristic of pyridine-2-thiones [31]. The O(1), C(9), and O(2) of the ester group are unfolded relative to the mean square plane of the pyridine fragment by 4.88(1)°. The N(3) atom has a pyramidal configuration, the sum of the valence angles is 347.29(17)°, the bond lengths at the N(3) atom are within the limits 1.424-1.439(3) Å. A special feature of the molecular structure of the compound is the formation of intramolecular hydrogen bonds N(2)–H···O(1) (N(2)–H(2N) 0.83(3), N(2)···O(1) 2.675(3) Å, N(2)–H(2N)–O(1) 137(2)°), closing a five-membered ring at O(1)C(9)C(4)C(5)N(2)H(2). This same hydrogen atom participates in the formation of a

series of intermolecular bonds with the nitrile group N(2)–(H)···N(4): N(2)–H(2N) 0.83(3), N(2)···N(4) 2.959(3) Å, N(2)–H(2N)···N(4) 131(2)° (the underlined atoms are linked with the initial by a variation of the symmetry *x*, *y* + 1, *z*), directed along the *y* crystallographic axis (Fig. 2).

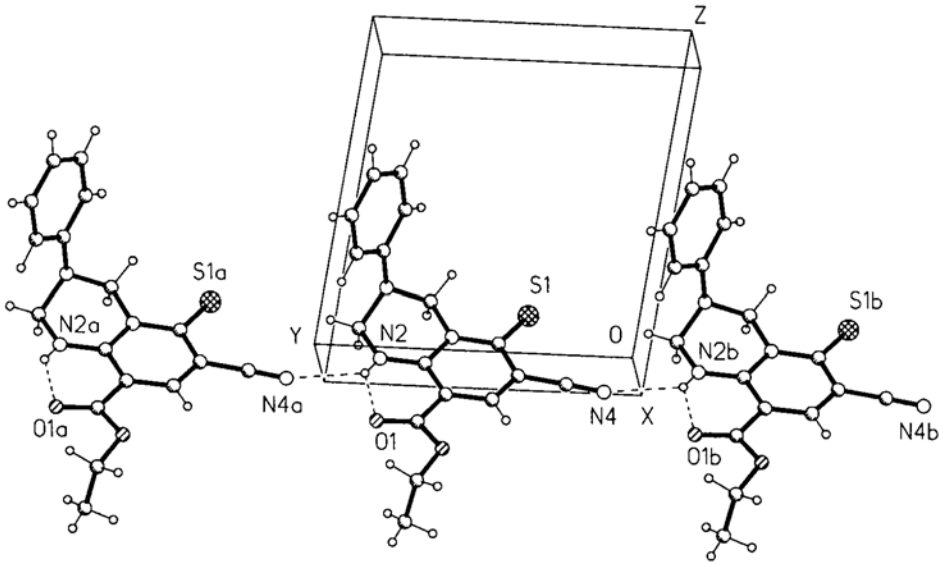


Fig. 2. Crystal packing of compound **3a**.

EXPERIMENTAL

The ^{1}H NMR spectra were taken on a Varian Gemini 200 instrument (200 MHz) in DMSO-d_6, internal standard was TMS. The IR spectra were obtained on an IKS-29 spectrophotometer (in nujol), elemental analysis was carried out on a Perkin-Elmer CHN analyzer. A check on the purity of the obtained substances was effected by TLC on Silufol UV-254 plates, eluent was acetone–heptane, 1 : 1, visualization with iodine vapor, UV detector. The melting points of substances were determined on a Kofler stage and are not corrected.

X-Ray Structural Investigation of a monocrystal of compound **3a** (grown in acetone–DMF, 1 : 1) of size 0.5 x 0.32 x 0.25 mm was carried out at room temperature on an Enraf-Nonius CAD-4 automatic four-circle diffractometer (MoKα radiation, λ = 0.71073 Å, ratio of scanning rates 2θ/ω 1.2, θ_{max} = 25°, segment of sphere $0 \le h \le 11$, $-11 \le k \le 11$, $-11 \le l \le 11$). In all 2745 reflections were collected. The crystals of compound **3a** were triclinic, a = 9.282(3), b = 9.411(2), c = 9.867(2) Å, α = 96.49(2), β = 106.59(3), γ = 98.40(3)°, V = 806.3(4) Å^3, M = 340.40, Z = 2, d_{calc} = 1.402 g/cm^3, μ = 0.219 mm^{-1}, F(000) = 356, space group $P\bar{1}$, (N 2). The structure was interpreted by the direct method and refined by the least squares method in a full matrix anisotropic approximation using the SHELXL97 and SHELXS97 set of programs [31, 32]. In the refinement 2086 reflections with $I > 2\sigma(I)$ were used (281 refined parameters, number of reflections per parameter 7.4). The positions of the hydrogen atoms were calculated geometrically and refined isotropically. The weighting scheme calculated from the following equation was used in the refinement $w = 1/[\sigma^2(Fo^2)+(0.0545P)^2 + 0.0871P]$, where $P = (Fo^2+2Fc^2)/3$. The final values of the divergence factors were R = 0.0353 and R_w = 0.0951, GOOF = 1.033. The residual electron density from the Fourier difference synthesis was -0.18 and 0.17 e/Å^2. Calculation of absorption in the crystal was carried out by the azimuthal scanning method. The complete set of X-ray structural data for compound **3a** is deposited in the Cambridge Structure Data Bank (No. CCDC 601358).

N-Methylmorpholinium 1-Amino-2,4-dicyano-4-ethoxycarbonyl-1,3-butadienethiolate (1) was obtained by a modification of the procedure of [15]. N-Methylmorpholine (6.5 ml, 60 mmol) was added to a suspension of the ethyl ester of *E*-2-cyano-3-ethoxyacrylic acid [33] (10 g, 59 mmol) and cyanothioacetamide [34] (5.9 g, 59 mmol) in EtOH (25 ml). The resulting dark-red solution was stirred for 5 h at ~20°C, left overnight, then an equal volume of ether was added to the obtained suspension, and the mixture stirred for 1 h at ~20°C. The orange crystalline solid butadienethiolate **1** was filtered off, washed with cold EtOH, and with ether. Yield 82%; mp 127-130°C (dec.) (Lit. 113-117°C [15]). IR spectrum, ν, cm^{-1}: 1629 (δ NH_2), 1689 (C=O), 2193 and 2217 (2 C≡N), 3300 and 3420 (NH_2). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 8.61 (1H, s, H-3); 8.05 and 7.18 (both 1H, br. s, NH_2); 4.10 (2H, q, *J* = 7.0, $C\underline{H}_2CH_3$); 3.78 (4H, m, CH_2OCH_2); 3.21 (4H, m, CH_2NCH_2); 2.82 (3H, s, NCH_3); 1.25 (3H, t, *J* = 7.0, $CH_2C\underline{H}_3$).

Pyrido[1,2-*a*][1,3,5]triazines 3a-e (General Method). A mixture of butadienethiolate **1** (1 g, 3.1 mmol), the appropriate amine **2a-e** (3.1 mmol), and 37% HCHO (5 ml) in EtOH (15-20 ml) was brought to boiling with stirring, and from the initially formed light-red solution a finely crystalline solid separated after several seconds. The reaction mixture was boiled for 3 min further with vigorous stirring, the obtained suspension was stirred for 2 h at ~20°C, the solid pyrido[1,2-*a*][1,3,5]triazine **3a-e** was filtered off, and washed with EtOH. For analytical purposes the product was recrystallized from a suitable solvent.

7-Cyano-3-phenyl-6-thioxo-1,3,4,6-2H-pyrido[1,2-*a*][1,3,5]triazine-9-carboxylic Acid Ethyl Ester (3a). Light-yellow crystals, yield 81%; mp 227-230°C (dec.) (Me_2CO : DMF, 1 : 1). IR spectrum, ν, cm^{-1}: 1685 (C=O), 2223 (C≡N), 3190 (NH). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 9.96 (1H, br. s, NH); 7.97 (1H, s, H-8); 7.32 (2H, m, C_6H_5, H-2,6); 7.00 (3H, m, C_6H_5, H-3-5); 6.08 (2H, br. s, 2H-4); 5.19 (2H, br. s, 2H-2); 4.25 (2H, q, *J* = 7.0, $C\underline{H}_2CH_3$); 1.36 (3H, t, *J* = 7.0, $CH_2C\underline{H}_3$). Found, %: C 59.30; H 4.78; N 16.60. $C_{17}H_{16}N_4O_2S$. Calculated, %: C 59.98; H 4.74; N 16.46.

7-Cyano-3-(3,4-dimethylphenyl)-6-thioxo-1,3,4,6-2H-pyrido[1,2-*a*][1,3,5]triazine-9-carboxylic Acid Ethyl Ester (3b). Yellow crystals, yield 73%; mp 207-209°C (Me_2CO : DMF, 4 : 1). IR spectrum, ν, cm^{-1}: 1675 (C=O), 2225 (C≡N), 3210 (NH). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 9.94 (1H, br. s, NH); 7.95 (1H, s, H-8); 6.98 (1H, d, *J* = 7.9, Ar, H-6); 6.78 (1H, br. s, Ar, H-2); 6.65 (1H, d, *J* = 7.9, Ar, H-5); 6.00 (2H, br. s, 2H-4); 5.12 (2H, br. s, 2H-2); 4.24 (2H, q, *J* = 7.1, $C\underline{H}_2CH_3$); 2.21 and 2.14 (both 3H, s, $2CH_3$); 1.34 (3H, t, *J* = 7.1, $CH_2C\underline{H}_3$). Found, %: C 61.88; H 5.49; N 15.28. $C_{19}H_{20}N_4O_2S$. Calculated, %: C 61.94; H 5.47; N 15.21.

7-Cyano-3-(2-furylmethyl)-6-thioxo-1,3,4,6-2H-pyrido[1,2-*a*][1,3,5]triazine-9-carboxylic Acid Ethyl Ester (3c). Yellow needle-shaped crystals, yield 85%; mp 211-213°C (DMF : EtOH, 1 : 1). IR spectrum, ν, cm^{-1}: 1675 (C=O), 2220 (C≡N), 3200 (NH). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 9.74 (1H, br. s, NH); 8.01 (1H, s, H-8); 7.47, 6.34, and 6.27 (all 1H, m, furyl); 5.39 (2H, br. s, 2H-4); 4.54 (2H, br. s, 2H-2); 4.28 (2H, q, *J* = 7.2, $C\underline{H}_2CH_3$); 2.84 (2H, s, $NC\underline{H}_2$-C_3H_4O); 1.34 (3H, t, *J* = 7.2, $CH_2C\underline{H}_3$). Found, %: C 56.03; H 4.71; N 16.13. $C_{16}H_{16}N_4O_3S$. Calculated, %: C 55.80; H 4.68; N 16.27.

7-Cyano-3-(4-fluorophenyl)-6-thioxo-1,3,4,6-2H-pyrido[1,2-*a*][1,3,5]triazine-9-carboxylic Acid Ethyl Ester (3d). Light-yellow crystals, yield 74%: mp 226-230°C (dec.) (DMF : EtOH, 1 : 1). IR spectrum, ν, cm^{-1}: 1676 (C=O), 2217 (C≡N), 3210 (NH). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 9.95 (1H, br. s, NH); 8.00 (1H, s, H-8); 7.02 (4H, m, 4-$FC_6\underline{H}_4$); 6.05 (2H, br. s, H_2-4); 5.14 (2H, br. s, H_2-2); 4.25 (2H, q, *J* = 7.1, $C\underline{H}_2CH_3$); 1.34 (3H, t, *J* = 7.1, $CH_2C\underline{H}_3$). Found, %: C 56.30; H 4.28; N 15.40. $C_{17}H_{15}FN_4O_2S$. Calculated, %: C 56.97; H 4.22; N 15.63.

7-Cyano-3-(2-ethoxyphenyl)-6-thioxo-1,3,4,6-2H-pyrido[1,2-*a*][1,3,5]thiazine-9-carboxylic Acid Ethyl Ester (3e). Yellow crystals, yield 83%; mp 225-227°C (decomp.) (from DMF : aqueous HCHO, 10 : 1). IR spectrum, ν, cm^{-1}: 1690 (C=O), 2230 (C≡N), 3175 (NH). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 9.93 (1H, br. s, NH); 8.03 (1H, s, H-8); 6.90 (2H, m, Ar, H-3,6); 6.72 (2H, m, Ar, H-4,5); 5.97 (2H, br. s, 2H-4); 5.06 (2H, br. s, 2H-2); 4.25 (2H, q, *J* = 7.1, $COOC\underline{H}_2CH_3$); 4.09 (2H, q, *J* = 6.9, $OC\underline{H}_2CH_3$); 1.45 (3H, t, *J* = 6.9, $OCH_2C\underline{H}_3$); 1.32 (3H, t, *J* = 7.1, $COOCH_2C\underline{H}_3$). Found, %: C 58.90; H 5.27; N 14.68. $C_{19}H_{20}N_4O_3S$. Calculated, %: C 59.36; H 5.24; N 14.57.

The work was carried out with the financial support of the Russian Fund for Fundamental Investigations (RFFI) (project 05-03-32031).

REFERENCES

1. V. V. Dotsenko, S. G. Krivokolysko, and V. P. Litvinov, *Izv. Akad. Nauk, Ser. Khim.*, 2605 (2005).
2. Haijian Shi, Z. Wang, and Haoxin Shi, *Synth. Commun.*, **29**, 2027 (1999).
3. Z. Wang, Haoxin Shi, and Haijian Shi, *Synth. Commun.*, **31**, 2841 (2001).
4. Z. Wang, T. You, Haijian Shi, and Haoxin Shi, *Molecules*, **1**, 89 (1996). Avail. URLs: http://www.mdpi.net/molecules/list96.htm; http://www.springerlink.com/.
5. Z. Wang, T. You, Hai-Jian Shi, and Hao-Xin Shi, *Gaodeng Xuexiao Huaxue Xuebao*, **18**, 550 (1997); *Chem. Abs.*, **127**, 95265 (1997).
6. Hao-Xin Shi, Hai-Jian Shi, and Z. Wang, *Youji Huaxue*, **20**, 344 (2000); *Chem. Abs.*, **133**, 120280 (2000).
7. S. Yadav Lal Dhar, A. Vaish, and S. Sharma, *J. Agric. Food Chem.*, **42**, 811 (1994); *Ref. Zh. Khim.*, 24Zh334 (1994).
8. Z. A. Hozein, A. O. S. Abd El-Wareth, H. A. H. El-Sherief, and A. M. Mahmoud, *Z. Naturforsch., B: Chem. Sci.*, **52**, 1401 (1997); *Chem. Abs.*, **128**, 88906 (1998).
9. Haijian Shi, Haoxin Shi, and Z. Wang, *J. Heterocycl. Chem.*, **38**, 929 (2001).
10. Haijian Shi, Z. Wang, and Haoxin Shi, *Chimia*, **51**, 529 (1997); *Ref. Zh. Khim.*, 13Zh272 (1998).
11. Z. A. Hozein, *J. Chem. Res. Synop.*, No. 3, 99 (2000).
12. V. V. Dotsenko, S. G. Krivokolysko, A. N. Chernega, and V. P. Litvinov, *Dokl. Akad. Nauk*, **389**, 763 (2003).
13. V. V. Dotsenko, S. G. Krivokolysko, and V. P. Litvinov, in *Abstracts of International Conference "Chemistry of Nitrogen Containing Heterocycles (CNCH-2003)"*, Kharkiv, 2003, p. 176.
14. V. P. Litvinov, *Usp. Khim.*, **72**, 75 (2003).
15. V. D. Dyachenko and R. P. Tkachev, *Zh. Org. Khim.*, **38**, 768 (2002).
16. M. T. Cocco, C. Congiu, and A. Maccioni, *J. Heterocycl. Chem.*, **27**, 1143 (1990).
17. M. T. Cocco, C. Congiu, A. Maccioni, and A. Plumitallo, *J. Heterocycl. Chem.*, **26**, 1859 (1989).
18. V. D. Dyachenko, R. P. Tkachev, and A. N. Chernega, *Khim. Geterotsikl. Soedin.*, 589 (2005). [*Chem. Heterocycl. Comp.*, **41**, 503 (2005)].
19. M. Tramontini, *Synthesis*, 703 (1973).
20. B. Stanovnik and M. Tišler, *Synthesis*, 308 (1972).
21. A. Fiksdahl and C. Wentrup, *ARKIVOK*, **1** (*iii*), 438 (2000). Avail. URL: http://www.arkat-usa.org/ark/journal/2000/I03_Jones/GJ-028E/copy.pdf
22. B. Zaleska, B. Trzewik, E. Stodolak, J. Grochowski, and P. Serda, *Synthesis*, 2975 (2004).
23. B. Zaleska, B. Trzewik, E. Stodolak, J. Grochowski, and P. Serda, *Synthesis*, 674 (2005) (errata & addenda).
24. Ya. G. Balon and V. A. Smirnov, *Zh. Org. Khim.*, **16**, 738 (1980).
25. Ya. G. Balon and V. A. Smirnov, *Zh. Org. Khim.*, **17**, 391 (1981).
26. Y. Watanabe, H. Usui, S. Kobayashi, H. Yoshiwara, T. Shibano, T. Tanaka, Y. Morishima, M. Yasuoka, and M. Kanao, *J. Med. Chem.*, **35**, 189 (1992).
27. D. Pawlak, K. Pawlak, E. Chabielska, J. Małyszko, A. Takada, M. Myśliwiec, and W. Buczko, *Thromb. Res.*, **90**, 259 (1998).
28. D. Pawlak, M. Adamkiewicz, J. Małyszko, A. Takada, M. Myśliwiec, and W. Buczko, *J. Cardiovasc. Pharmacol.*, **32**, 266 (1998).

29. R. J. Bochis, GB Patent 1503046 (1978). Avail. URL: http://ep.espacenet.com/.
30. R. J. Bochis, US Patent 3984549 (1976). Avail. URL: http://patft.uspto.gov/netahtml/srchnum.htm.
31. G. M. Sheldrick, *SHELXS 97 (1997). Program for the Solution of Crystal Structure*, Univ. of Göttingen, Göttingen, Germany.
32. G. M. Sheldrick, *SHELXL 97 (1997). Program for the Refinement of Crystal Structures*, Univ. of Göttingen, Göttingen, Germany.
33. V. V. Mezheritskii, E. P. Olekhnovich, S. M. Lukyanov, and G. M. Dorofeenko, *Orthoesters in Organic Synthesis* [in Russian], Izd. Rost. Univ., Rostov-on-Don (1976), p. 94.
34. J. S. A. Brunskill, A. De, and D. F. Ewing, *J. Chem. Soc., Perkin Trans. 1*, 629 (1978).