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Synthesis and Reactions of Pyrazole-4-carbaldehydes

E. V. Rudyakova, V. A. Savosik, L. K. Papernaya, A. I. Albanov, I. T. Evstaf'eva, and G. G. Levkovskaya

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

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Abstract—1-, 3-, and 5-Alkylpyrazoles, as well as linearly bridged bis-pyrazoles, were converted into the corresponding 4-formyl derivatives by Vilsmeier–Haak reaction both under standard conditions and under microwave activation in DMF over a period of 10 min. 1,1′-(Hexane-1,6-diyl)bis(3,5-dimethyl-1*H*-pyrazole) and 1,1′-(benzene-1,4-diyldimethylene)bis(3,5-dimethyl-1*H*-pyrazole) gave rise to 4-formyl derivatives at both pyrazole rings. 5-Chloro-1,3-dialkyl-1*H*-pyrazoles failed to undergo formylation according to Vilsmeier–Haak or under microwave activation. 1,1′-Bridged bis-3,5-dimethyl-1*H*-pyrazoles reacted with 2-sulfanylethanol on heating in the presence of chloro(trimethyl)silane to give the corresponding bridged bis-4-(1,4,6-oxadithiocan-5-yl)-1*H*-pyrazoles.

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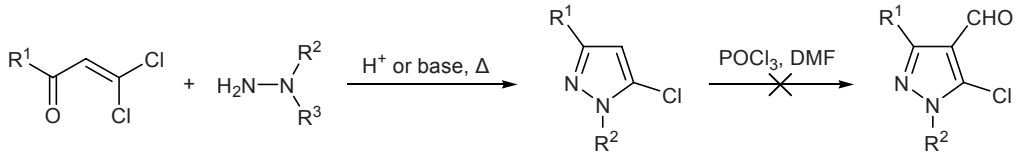
Pyrazoles belong to one of the most important classes of heterocyclic compounds which are very significant for medicinal chemistry [1]. Molecules of many modern drugs, e.g., antiphlogistic, antidiabetic, analgesic, etc., as well as of insectoacaricides used in practice, contain pyrazole ring as structural fragment [1, 2].

In continuation of our studies on the synthesis and properties of pyrazoles and halopyrazoles derived from chloro enones [3, 4], in the present work we examined formylation of 5-chloropyrazoles and linearly bridged bis-pyrazoles according to Vilsmeier–Haak. Introduction of an aldehyde group into pyrazole molecule was expected to ensure intramolecular heterocyclizations with formation of fused or linearly linked heterocyclic compounds [5]. From this viewpoint, the synthetic potential of halogen-substituted pyrazolecarbaldehydes is difficult to overestimate [6]. For example, various linear and fused polyheterocyclic systems were synthesized from 5-chloro-3-methyl-1-phenyl-1*H*-pyrazole-4-carbaldehyde and typical reagents for carbonyl group, such as hydrazines, hydroxylamine, and thiosemicarbazide, as well as diamines of the aliphatic and aromatic series [6].

It is known that 1-unsubstituted, 1-alkyl-, and 1-phenyl-3-alkyl-4-formyl-5-chloro(bromo)pyrazoles are formed by reactions of the corresponding pyrazol-5-ones with phosphoryl chloride or bromide in dimethylformamide (Vilsmeier–Haak reaction) [6–8]. Presumably, the initial step is introduction of a formyl group into pyrazol-5-one (5-hydroxypyrazole), and next follows halogenation of 4-formylpyrazol-5-one by the action of $POHlg_3$. This reaction scheme is supported by the fact that pyrazol-5-ones are converted into 5-halopyrazoles by reaction with phosphoryl chloride under severe conditions. For example, 5-chloro-(bromo)pyrazoles were synthesized for the first time by heating pyrazol-5-ones with phosphoryl chloride or bromide for 9–12 h at 100–130°C in a sealed ampule

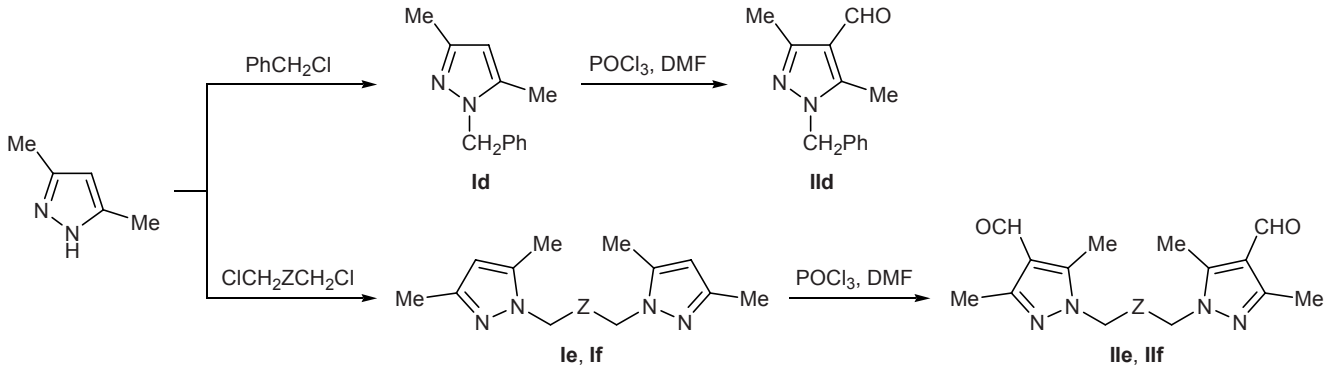
Scheme 1.



Ia–Ic

$R^1 = R^2 = R^3 = Me$ (**a**); $R^1 = Pr$, $R^2 = Me$, $R^3 = Me$ (**b**); $R^1 = Me$, $R^2 = Et$, $R^3 = H$ (**c**).

Scheme 2.



Z = $(CH_2)_4$ (**e**), 1,4-C_6H_4 (**f**).

[9]. This procedure was then widely used for the preparation of halopyrazoles from pyrazolones, and only reaction conditions, halogenating agents, and solvents were varied [10–12].

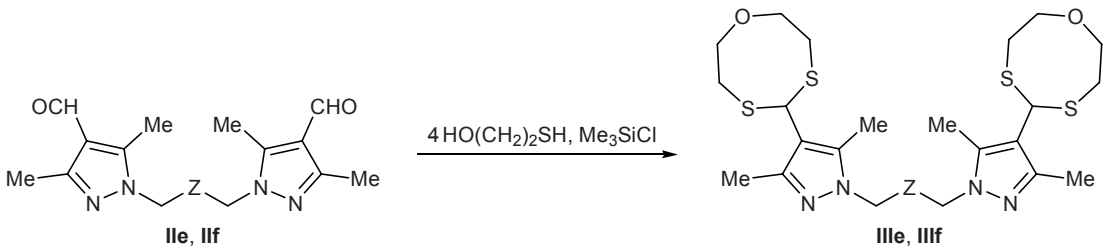
However, we failed to obtain 1,3-dialkyl-5-chloro-1*H*-pyrazole-4-carbaldehydes by Vilsmeier–Haak reaction of 1,3-dialkyl-5-chloro-1*H*-pyrazoles **Ia**–**Ic** prepared from alkyl 2,2-dichlorovinyl ketones and alkyl or 1,1-dialkylhydrazines [3] (Scheme 1). The reactions were carried under the conditions described in [6–8], but neither raising the temperature nor increasing the reaction time led to the formation of desired products. 5-Chloropyrazoles **Ia**–**Ic** also failed to react with phosphoryl chloride or bromide in DMF under microwave activation.

We then tried to effect formylation of pyrazoles **Id**–**If** which were synthesized by alkylation of 3,5-dimethyl-1*H*-pyrazole with the corresponding halogen derivatives in DMSO in the presence of alkali [13] (Scheme 2). Unlike the procedure reported in [13], we used considerably lesser amount of the solvent (by a factor of more than 10), and heating of the reaction mixture was avoided. The yields of N-substituted pyrazoles **Id**–**If** were 84–87%.

Unlike chloropyrazoles **Ia**–**Ic**, 1-benzyl-3,5-dimethyl-1*H*-pyrazole (**Id**) and newly synthesized bis-pyrazoles **Ie** and **If** readily reacted with phosphoryl chloride in DMF under mild conditions to give the corresponding 4-formyl derivatives in good yields. By carrying out these reactions under microwave irradiation we succeeded in considerably shortening the reaction time. The yields of pyrazole-4-carbaldehydes **IId**–**IIf** were 52 to 84% (Scheme 2). The structure of compounds **Id**–**If** and **IId**–**IIf** was confirmed by IR and NMR spectra and elemental analyses.

Bis-pyrazoles **IIe** and **IIf** were brought into reaction with 2-sulfanylethanol in the presence of chloro(trimethyl)silane with a view to obtain new polyfunctional pyrazole derivatives and develop new procedures for the protection of aldehyde group. We previously showed [14–16] that aldehydes of the thiophene series react with alkanethiols and dithiols in the presence of Me_3SiCl under mild conditions to give the corresponding acyclic and cyclic dithioacetals. The reactions of pyrazolecarbaldehydes **IIe** and **IIf** with 2-sulfanylethanol were carried out using 10-fold excess of Me_3SiCl (reaction time 2–4 h). However, unlike aldehydes of the thiophene series [14–16], the reactions with aldehydes **IIe** and **IIf** required elevated temperature (50–70°C), and the products were previously unknown 1,4,6-oxadithiocane derivatives **IIIe** and **IIIf** (Scheme 3). It is known that 2-sulfanylethanol and

Scheme 3.



Z = $(CH_2)_4$ (**e**), 1,4-C_6H_4 (**f**).

3-sulfanylpropan-1-ol react with aliphatic and aromatic aldehydes in the presence of scandium trifluoromethanesulfonate [17], boron trifluoride [18], or *p*-toluenesulfonic acid [19] to afford the expected 1,3-oxathiolanes and 1,3-oxathianes. No corresponding pyrazolyloxathiolanes were formed when the reactions were performed in excess Me_3SiCl at a pyrazolecarbaldehyde-to-2-sulfanylethanol ratio of 1:2; in this case we isolated a mixture of unreacted pyrazole **II** and compound **III**.

According to our previous data [14, 16], chloro(trimethyl)silane facilitates protonation of the carbonyl group in thiophenecarbaldehydes, thus favoring thioacetalization. In addition, Me_3SiCl acts as dehydrating agent which effectively binds liberated water and ensures selective formation of 1,3-dithiolanes and 1,3-dithianes. In the reactions with compounds **IIe** and **IIf** each carbonyl group binds two molecules of 2-sulfanylethanol, and the subsequent heterocyclization yields 1,4,6-oxadithiocane derivatives **IIIe** and **IIIf**. The observed reaction direction may be determined by electronic and steric effects of the neighboring methyl groups in positions *3* and *5* of the pyrazole ring.

The structure of compounds **IIIe** and **IIIf** was confirmed by spectral and analytical methods. The IR spectra of **IIIe** and **IIIf** lacked carbonyl absorption bands typical of initial bis-pyrazoles **IIe** and **IIf**, but absorption bands appeared in the region 1020–1043 cm^{-1} due to vibrations of the oxadithiocane fragment. Unlike bis-pyrazoles **IIe** and **IIf**, no signal assignable to aldehyde proton was present in the ^1H NMR spectra of **IIIe** and **IIIf**.

Taking into account that several simple and effective methods, including solvent-free procedures [20], have been proposed for deprotection of carbonyl groups, pyrazoles **IIIe** and **IIIf** may be used as intermediate products for further transformations.

To conclude, we have developed convenient preparative procedures for the synthesis of previously unknown pyrazole- and bis-pyrazolecarbaldehydes and 2-(pyrazol-4-yl)-1,4,6-oxadithiocanes. The newly synthesized compounds attract interest as potential biologically active substances, as well as precursors and reagents for the design of complex polyfunctional structures.

EXPERIMENTAL

The IR spectra were recorded on a Varian-3100 spectrometer with Fourier transform using an ATR (attenuated total reflectance) adapter. The ^1H and ^{13}C NMR spectra were measured on a Bruker DPX-400 instrument at 400.13 and 101.61 MHz, respectively, using HMDS as internal reference. The chemical shifts were determined with an accuracy of ±0.01 (^1H) and ±0.02 ppm (^{13}C), and the ^1H–^1H coupling constants were determined with an accuracy of ±0.1 Hz. Microwave-assisted reactions were performed in a Samsung microwave furnace (800 W, 2450 MHz).

5-Chloro-1,3-dimethyl-1*H*-pyrazole (**Ia**) and 5-chloro-1-methyl-3-propyl-1*H*-pyrazole (**Ib**) were synthesized by reactions of 1,1-dimethylhydrazine with 1,1-dichlorobut-1-en-3-one and 1,1-dichlorohex-1-en-3-one, respectively; 5-chloro-1-ethyl-3-methyl-1*H*-pyrazole (**Ic**) was prepared from 1,1-dichlorobut-1-en-3-one and ethylhydrazine according to the procedure described in [3]. The physical constants of chloropyrazoles **Ia**–**Ic** were consistent with published data.

1-Benzyl-3,5-dimethyl-1*H*-pyrazole (Id). A mixture of 11.20 g (0.2 mol) of potassium hydroxide and 10 ml of dimethyl sulfoxide was stirred for 10 min, 9.61 g (0.1 mol) of 3,5-dimethyl-1*H*-pyrazole was added, and the mixture was stirred for 20 min at 20–22°C. Benzyl chloride, 15.19 g (0.12 mol), was slowly added at such a rate that the temperature did not exceed 30°C, and the mixture was stirred for 3 h at 20–22°C, poured into 100 ml of cold water, and extracted with diethyl ether. The extract was dried over $MgSO_4$ and evaporated, and the residue was distilled under reduced pressure. Yield 16.20 g (87%), bp 191–193°C (20 mm). IR spectrum, ν, cm^{-1}: 3121 (=C–H, pyrazole), 3025 (=C–H, Ph), 2979, 2918, 2861 (C–H, aliph.), 1634 (C=C, C=N). ^1H NMR spectrum (CCl_4), δ, ppm: 1.97 s (3H, CH_3), 2.13 s (3H, CH_3), 4.98 s (2H, CH_2), 5.62 s (1H, 4-H), 6.95 m and 7.19 m (5H, C_6H_5). Found, %: C 77.58; H 7.57; N 14.99. $C_{12}H_{14}N_2$. Calculated, %: C 77.38; H 7.58; N 15.04.

1,1′-(Hexane-1,6-diyl)bis(3,5-dimethyl-1*H*-pyrazole) (Ie) was synthesized in a similar way from 9.61 g (0.1 mol) of 3,5-dimethyl-1*H*-pyrazole and 9.30 g (0.06 mol) of 1,6-dichlorohexane using 11.20 g (0.2 mol) of potassium hydroxide. Yield 11.52 g (84%), bp 192–196°C (15 mm). IR spectrum, ν, cm^{-1}: 3125 (=C–H, pyrazole), 2928, 2862 (C–H, aliph.), 1639, 1549 (C=C, C=N). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.29 br.s (4H, CH_2), 1.74 br.s (4H, CH_2), 2.17 br.s (12H, CH_3), 3.88 t (4H, NCH_2), 5.72 s (2H, 4-H). Found, %: C 70.12; H 9.52; N 20.44. $C_{16}H_{26}N_4$. Calculated, %: C 70.03; H 9.55; N 20.42.

1,1′-(Benzene-1,4-diyldimethylene)bis(3,5-dimethyl-1*H*-pyrazole) (If) was synthesized in a similar

way from 9.61 g (0.1 mol) of 3,5-dimethyl-1*H*-pyrazole and 10.50 g (0.06 mol) of 1,4-bis(chloromethyl)benzene using 11.20 g (0.2 mol) of potassium hydroxide. The reaction mixture was poured into 100 ml of cold water, and the precipitate was filtered off and dried in air. Yield 12.62 g (86%), mp 95–97°C. IR spectrum, ν, cm^{-1}: 3121 (=C–H, pyrazole), 3025 (=C–H_{arom}), 2979, 2918, 2861 (C–H, aliph.), 1634, 1547 (C=C, C=N). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.10 s (6H, CH_3), 2.20 s (6H, CH_3), 5.14 s (4H, NCH_2), 5.80 s (2H, 4-H), 6.97 s (4H, C_6H_4). Found, %: C 73.40; H 7.52; N 19.08. $C_{18}H_{22}N_4$. Calculated, %: C 73.44; H 7.53; N 19.03.

1,3-Dimethyl-1*H*-pyrazole-4-carbaldehydes IId–IIf (*general procedure*). *a*. 1-Substituted 3,5-dimethyl-1*H*-pyrazole **Id**–**If**, 0.1 mol, was dissolved in 11 g (0.15 mol) of dimethylformamide, 23 g of phosphoryl chloride was added dropwise, and the mixture was stirred for 5 h at 70–75°C, poured into 200 ml of cold water, and neutralized with a saturated solution of sodium hydrogen carbonate to pH 7–8. The precipitate was filtered off and dried in air.

b. A mixture of 0.1 mol of dimethylpyrazole **Id**–**If**, 20 ml of DMF, and 23 g of $POCl_3$, prepared in a one-neck flask equipped with a reflux condenser, was placed in a microwave furnace and irradiated over a period of 10 min. The mixture was then treated as described above in *a*.

1-Benzyl-3,5-dimethyl-1*H*-pyrazole-4-carbaldehyde (IId) was synthesized from 18.63 g (0.1 mol) of pyrazole **Id**. Yield 11.60 g (54%) (*a*), 10.70 g (50%) (*b*); mp 66–68°C. IR spectrum, ν, cm^{-1}: 3045 (=C–H, Ph), 2957, 2859, 2823, 2739 (C–H, aliph.), 1670 (C=O), 1547 (C=C, C=N). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.42 s (6H, CH_3), 5.21 s (2H, NCH_2), 7.11 d and 7.28 m (5H, C_6H_5), 9.88 s (1H, CHO). ^{13}C NMR spectrum, δ_C, ppm: 10.27 and 12.59 (CH_3), 52.74 (NCH_2), 126.92, 128.12, 129.02, 135.71 (Ph), 118.59, 144.50, 151.13 (pyrazole), 184.92 (C=O). Found, %: C 72.81; H 6.56; N 13.09. $C_{13}H_{14}N_2O$. Calculated, %: C 72.87; H 6.59; N 13.07.

1,1′-(Hexane-1,6-diyl)bis(3,5-dimethyl-1*H*-pyrazole-4-carbaldehyde) (IIe) was synthesized from 13.72 g (0.05 mol) of compound **Ie**. Yield 8.60 g (52%) (*a*), 8.92 g (54%) (*b*); mp 85–86°C. IR spectrum, ν, cm^{-1}: 2939, 2858, 2814, 2734 (C–H, aliph.), 1665 (C=O), 1541 (C=C, C=N). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.32 br.s (2H, CH_2), 1.79 br.s (2H, CH_2), 2.41 s (6H, CH_3), 2.47 s (6H, CH_3), 3.95 t (2H, NCH_2), 9.88 s (2H, CHO). ^{13}C NMR spectrum, δ_C, ppm: 9.83, 12.16 (CH_3), 25.98, 29.34 (CH_2), 48.11 (NCH_2), 117.69, 143.41, 150.69 (pyrazole), 184.59 (C=O). Found, %: C 65.68; H 8.32; N 16.58. $C_{18}H_{26}N_4O_2$. Calculated, %: C 65.41; H 7.94; N 16.96.

1,1′-(Benzene-1,4-diyldimethylene)bis(3,5-dimethyl-1*H*-pyrazole-4-carbaldehyde) (IIf) was synthesized from 14.72 g (0.05 mol) of compound **If**. Yield 14.91 g (85%) (*a*), 14.20 g (81%) (*b*); mp 151–153°C. IR spectrum, ν, cm^{-1}: 3045 (=C–H_{arom}), 2955, 2855, 2820, 2738 (C–H, aliph.), 1667 (C=O), 1540 (C=C, C=N). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.42 s (6H, CH_3), 2.43 s (6H, CH_3), 5.19 s (4H, NCH_2), 7.07 s (4H, C_6H_4), 9.89 s (2H, CHO). ^{13}C NMR spectrum, δ_C, ppm: 9.92, 12.25 (CH_3), 51.87 (NCH_2), 127.20, 135.32 (C_6H_4), 118.21, 144.15, 150.87 (pyrazole), 184.56 (C=O). Found, %: C 69.00; H 6.59; N 16.43. $C_{20}H_{22}N_4O_2$. Calculated, %: C 68.54; H 6.33; N 16.00.

1,1′-(Hexane-1,6-diyl)bis[3,5-dimethyl-4-(1,4,6-oxadithiocan-5-yl)-1*H*-pyrazole] (IIIe). 2-Sulfanylethanol, 0.63 g (8 mmol), was added dropwise under stirring and heating to a mixture of 0.66 g (2 mmol) of compound **IIe** and 2.5 ml of chloro(trimethyl)silane. The mixture was vigorously stirred for 4 h at 50–70°C and cooled, and the precipitate was filtered off, washed with cold hexane, and dried under reduced pressure. Yield 1.05 g (92%), white powder, mp 144–146°C. IR spectrum, ν, cm^{-1}: 2953, 2922, 2870, 2859 (C–H), 1545 (C=C, C=N), 1041, 1020 (C–O–C). ^1H NMR spectrum (CD_3OD), δ, ppm: 1.42 m (4H, CH_2), 1.89 m (4H, CH_2), 2.53 s and 2.55 s (6H each, CH_3), 2.71 d.t and 2.83 d.t (4H each, SCH_2, ^2J = 13.69, ^3J = 6.36 Hz), 3.73 d.t and 3.76, d.t (4H each, OCH_2, ^2J = 11.37, ^3J = 6.6 Hz), 4.32 t (4H, NCH_2, ^3J = 7.09 Hz), 5.47 s (2H, SCHS). ^{13}C NMR spectrum, δ_C, ppm: 10.74, 10.38 (CH_3), 26.72 (CH_2), 30.09 (CH_2), 36.24 (SCH_2), 43.73 (SCHS), 49.78 (NCH_2), 62.88 (OCH_2), 119.99, 145.08, 144.97 (pyrazole). Found, %: C 54.41; H 7.35; N 9.91; S 22.43. $C_{26}H_{42}N_4O_2S_4$. Calculated, %: C 54.92; H 7.04; N 9.85; S 22.69.

1,1′-(Benzene-1,4-diyldimethylene)bis[3,5-dimethyl-4-(1,4,6-oxadithiocan-5-yl)-1*H*-pyrazole] (IIIf) was synthesized in a similar way from 0.70 g (2 mmol) of compound **IIf** and 0.63 g (8 mmol) of 2-sulfanylethanol in 2.5 ml of Me_3SiCl. Excess Me_3SiCl was removed under reduced pressure, the light yellow oily residue was treated with ethanol, and the solvent was removed by decanting. The solution was evaporated. Yield 1.0 g (86%), light yellow thick waxy material. IR spectrum, ν, cm^{-1}: 3059 (C–H_{arom}), 2946, 2917, 2867, 2739 (C–H_{aliph}), 1545 (C=C, C=N), 1043 (C–O–C). ^1H NMR spectrum, δ, ppm: 2.44 s and

2.43 s (6H each, CH_3), 2.65 m and 2.77 m (4H each, SCH_2), 3.66 m (8H, OCH_2), 5.55 s (4H, NCH_2), 5.41 s (2H, SCHS), 7.28 s (4H, C_6H_4). ^{13}C NMR spectrum, δ_C, ppm: 10.62, 10.81 (CH_3), 36.21 (SCH_2), 43.49 (SCHS), 52.53 (NCH_2), 62.75 (OCH_2), 129.29, 135.43 (C_6H_4), 120.55, 145.60 (pyrazole). Found, %: C 57.33; H 6.06; N 9.41; S 21.93. $C_{28}H_{38}N_4O_2S_4$. Calculated, %: C 57.14; H 6.12; N 9.52; S 21.76.

REFERENCES

1. Elguero, J., Goya, P., Jagerovic, N., and Silva, A.M.S., *Targets in Heterocyclic Systems. Chemistry and Properties*, Attanasi, O.A. and Spinelli, D., Eds., Roma: Italian Soc. Chem., 2002, vol. 6, p. 53.
2. Grapov, A.F., *Usp. Khim*., 1999, vol. 68, p. 773.
3. Levkovskaya, G.G., Bozhenkov, G.V., Malyushenko, R.N., and Mirskova, A.N., *Russ. J. Org. Chem*., 2001, vol. 37, p. 1795; Levkovskaya, G.G., Bozhenkov, G.V., Larina, L.I., and Mirskova, A.N., *Russ. J. Org. Chem*., 2002, vol. 38, p. 1501; Bozhenkov, G.V., Levkovskaya, G.G., Mirskova, A.N., Dolgushin, G.V., Larina, L.I., and Ushakov, P.E., *Russ. J. Org. Chem*., 2003, vol. 39, p. 1069; Levkovskaya, G.G., Bozhenkov, G.V., Mirskova, A.N., and Tantsyrev, A.P., Russian Patent no. 2186772, 2002; *Byull. Izobret*., 2002, no. 22; Bozhenkov, G.V., Levkovskaya, G.G., Larina, L.I., Ushakov, P.E., Dolgushin, G.V., and Mirskova, A.N., *Russ. J. Org. Chem*., 2004, vol. 40, p. 1583; Bozhenkov, G.V., Savosik, V.A., Mirskova, A.N., and Levkovskaya, G.G., *Russ. J. Org. Chem*., 2008, vol. 44, p. 184.
4. Kondrashov, E.V., Rozentsveig, I.B., Sarapulova, G.I., Larina, L.I., Levkovskaya, G.G., Savosik, V.A., Bozhenkov, G.V., and Mirskova, A.N., *Russ. J. Org. Chem*., 2005, vol. 41, p. 735; Bozhenkov, G.V., Savosik, V.A., Larina, L.I., Mirskova, A.N., and Levkovskaya, G.G., *Russ. J. Org. Chem*., 2006, vol. 42, p. 901; Savosik, V.A., Bozhenkov, G.V., Mirskova, A.N., and Levkovskaya, G.G., *Russ. J. Org. Chem*., 2006, vol. 42, p. 1507.
5. Bratenko, M.K., Kadel'nik, Yu.V., Chornous, V.A., and Vovk, M.V., *Russ. J. Org. Chem*., 2008, vol. 44, p. 247.
6. Pawer, A. and Patil, A.A., *Indian J. Chem*., 1994, vol. 33, p. 156.
7. Malhotra, M., Falt-Hansen, B., and Becher, J., *J. Heterocycl. Chem*., 1991, vol. 28, p. 1837.
8. Wang, X.J., Tan, J., and Grozinger, K., *Tetrahedron Lett*., 2000, vol. 41, p. 4713.
9. Michaelis, A. and Dorn, H., *Chem. Ber*., 1907, vol. 23, p. 179;* Michaelis, A. and Dorn, H., *Justus Liebigs Ann. Chem*., 1907, vol. 325, p. 163;* Auwers, K. and Niemyer, F., *J. Prakt. Chem*., 1925, vol. 110, p. 153.
10. Butler, D.E. and De Wald, H.A., *J. Org. Chem*., 1971, vol. 36, p. 2542.
11. Habraken, C.L. and Moore, J.A., *J. Org. Chem*., 1965, vol. 30, p. 1892.
12. Fray, M.J., Bull, D.J., Cooper, K., Parry, M.J., and Stefaniak, M.H., *J. Med. Chem*., 1995, vol. 38, p. 3524.
13. Potapov, A.S., Domina, G.A., Khlebnikov, A.I., and Ogorodnikov, V.D., *Eur. J. Org. Chem*., 2007, p. 5112.
14. Papernaya, L.K., Levanova, E.P., Sukhomazova, E.N., Albanov, A.I., and Deryagina, E.N., *Russ. J. Org. Chem*., 2003, vol. 39, p. 1533.
15. Papernaya, L.K., Levanova, E.P., Sukhomazova, E.N., Albanov, A.I., and Deryagina, E.N., *Russ. J. Org. Chem*., 2005, vol. 41, p. 952.
16. Papernaya, L.K., Levanova, E.P., Sukhomazova, E.N., Albanov, A.I., and Deryagina, E.N., *Russ. J. Org. Chem*., 2006, vol. 42, p. 256.
17. Karimi, B. and Ma'mani, L., *Synthesis*, 2003, no. 16, p. 2503.
18. Wilson, G.E., Hvang, J., and Schloman, W.W., *J. Org. Chem*., 1968, vol. 33, p. 2133.
19. Stuparu, M., Grosu, I., Muntean, L., Ple, G., Cismas, C., Terec, A., Nan, A., and Mager, S., *Monatsh. Chem*., 2004, vol. 135, p. 89.
20. Wang, E.-C., Wu, C.-H., Chien, S.-C., Chiang, W.-C., and Kuo, Y.-H., *Tetrahedron Lett*., 2007, vol. 48, p. 7706; Oksdath-Mansilla, G. and Penenory, A.B., *Tetrahedron Lett*., 2007, p. 6150.

* Invalid reference.—*Publisher.*