2-Cyano-(2*E*,4)-pentadienoic acid (1). Freshly distilled acrolein (6.3 g, 0.11 mol) was added over 20 min at 10°C to a solution of $NCCH_2CO_2K$ (12.3 g, 0.1 mol) in 1 *M* aqueous NaH_2PO_4 (pH 5.4). The mixture was stirred for 2 h at 10—15°C and kept overnight, and then 30% H_2SO_4 was added at 5—10°C to pH 2.5. The precipitate that formed was separated, washed with toluene, and dissolved in ether. The solution was dried with $MgSO_4$ and concentrated, and the product was crystallized from ether to give 3.9g of acid **1**, m.p. 131—132°C (decomp.). IR, ν/cm: 1578, 1615 (C=C), 1682, 1703 sh. (C=O), 2233 (C≡N). ^{1}H NMR, δ: 6.00 (ddd, 1 H, H(3), $J_{H(3)H(2)}$= 10 Hz, $J_{H(3),H(4)}$= 1.4 Hz, $J_{H(3),H(1)}$= 0.6 Hz); 6.25 (ddd, 1 H, H(4), $J_{H(4),H(2)}$= 16.7 Hz, $J_{H(4),H(3)}$= 1.4 Hz, $J_{H(4),H(1)}$= 0.8 Hz); 6.89 (ddd, 1 H, H(2), $J_{H(2),H(4)}$= 16.7 Hz, $J_{H(2),H(1)}$= 11.4 Hz, $J_{H(2),H(3)}$= 10 Hz); 7.94 (ddd, 1 H, H(1), $J_{H(1),H(2)}$= 11.4 Hz, $J_{H(1),H(4)}$= 0.8 Hz, $J_{H(1),H(3)}$= 0.6 Hz); 9.51 (br.s, 1 H, COOH). Found (%): C, 58.51; H, 3.90; N, 11.33. $C_6H_5NO_2$. Calculated (%): C, 58.53, H, 4.09; N, 11.37.

2-Cyanopenta-(2*E*,4)-dienamide (2). Freshly distilled acrolein (4.2 g, 75 mmol) was added dropwise at 3—5°C to a solution of cyanoacetamide (4.2 g, 50 mmol) in 35 mL of 1 *M* aqueous K_3PO_4 (pH 7). The mixture was stirred for 2 h at 10—15°C and 1 h at 20°C. The precipitate that formed was separated, washed with cold water on a filter, and dried in a vacuum desiccator over P_2O_5 to give 2.4g of amide **2**, m.p. 140—145°C (decomp.) IR: 1392 (C—N), 1579, 1610 (C=O), 2223 (C≡N), 3407 (NH). ^{1}H NMR, δ: 6.31 (m, 2 H, H(3), H(4)); 7.08 (m, 1 H, H(2); 7.45 (br.s, 2 H, NH_2); 8.1 (d, 1 H, H(1), *J*= 12.0 Hz). Found (%): C, 58.84; H, 5.03; N, 23.10. $C_6H_6N_2O$. Calculated (%): C, 59.00; H, 4.95; N, 22.94.

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Received September 9, 1997;
in revised form October 27, 1997

Regioselective synthesis and properties of 3-cyano-6-thienylpyridine-2(1*H*)-thiones

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Reactions of sodium derivatives of 2- and 3-thenoylacetaldehydes with cyanothioacetamide gave 2- and 3-cyano-6-thienylpyridine-2(1*H*)-thiones, which were used in the synthesis of substituted 2-alkylthiopyridines, thieno[2,3-*b*]pyridines, and other fused heterocycles.

Key words: cyanothioacetamide, β-oxoaldehydes, 6-thienylpyridine-2(1*H*)-thiones, thieno[2,3-*b*]pyridines.

Previously, reactions of sodium derivatives of aroyl- and nicotinoylacetaldehyde with cyanothioacetamide were studied.[1—3] It was found that these reactions occur highly regioselectively to give 6-aryl- or 6-(3-pyridyl)-3-cyanopyridine-2(1*H*)-thiones. The compounds obtained were then used in the syntheses of difficultly accessible annelated heterocycles.[2]

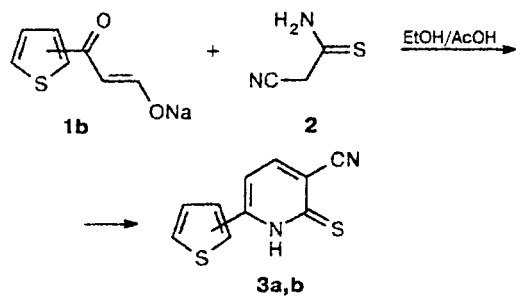
Taking into account that compounds of practical utility (pesticides, drugs, antioxidants, dyes, analytical reagents, *etc.*) have been found among substituted 3-cyanopyridine-2(1*H*)-thiones,[4] we have elaborated a convenient method for the synthesis of previously unknown 3-cyano-6-thienylpyridine-2(1*H*)-thiones and, on the basis of them, 2-alkylthiopyridines and fused pyridines. In addition, the study of the regioselectivity of reactions of cyanoacetic acid derivatives with 1,3-dicarbonyl compounds[1,5] was continued in this work.

Reactions of sodium derivatives of 2- and 3-thenoylacetaldehyde (**1a,b**) with cyanoacetamide (**2**) in ethanol in the presence of acetic acid occur regioselectively to give the corresponding 3-cyano-6-thienylpyridine-2(1*H*)-thiones **3a** and **3b**.

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 2, pp. 365—368, February, 1998.

1066-5285/98/4702-0357 $20.00

Scheme 1



1a, 3a: 2-thienyl; **1b, 3b:** 3-thienyl

The IR spectra of compounds **3a,b** contain absorption bands of the nitrile and thionamide groups at 2225—2226 and 1150—1183 cm^{-1}, respectively. In addition to characteristic signals for the protons of the thiophene moiety and the NH group, the ^1H NMR spectra of compounds **3a,b** contain signals for the protons of the pyridine ring, C(4)H and C(5)H, as two doublets at δ 7.20—7.22 and 8.18—8.20 with spin-spin coupling constant ^3J = 7.6—7.8 Hz. Such a magnitude of the coupling constant suggests that the thienyl substituent is located at position 6 of pyridine-2(1*H*)-thiones, because for 4-substituted pyridines, ^3J = 4.88 Hz. Similar regioselectivity was previously observed in reactions of cyanothio(seleno)acetamides with other β-oxoaldehydes,[1—3] as confirmed by the results of physicochemical analyses and X-ray diffraction studies of the previously synthesized 6-aryl-3-cyanopyridine-2(1*H*)-thiones.[1—3] Probably, the higher electrophilicity of the aldehyde carbon atom compared to the ketone carbon atom[1] is responsible for this direction of the reaction.

The chemical properties of the resulting pyridines **3a,b** also confirm their structure.

Compounds **3a,b** react chemoselectively with halocarbonyl compounds to give 2-alkylthiopyridines (**5a,b**). Compounds **5a** (R_1 = H) undergo the Thorpe—Ziegler reaction in the presence of KOH in DMF to give 3-aminothieno[2,3-*b*]pyridines (**6a**). Taking into consideration the large number of works on the synthesis of substituted 3-aminothieno[2,3-*b*]pyridines[4] from substituted 3-cyanopyridine-2(1*H*)-thiones and halocarbonyl compounds, one can conclude that this has become a qualitative reaction for these compounds. The properties of the products obtained are listed in Tables 1 and 2.

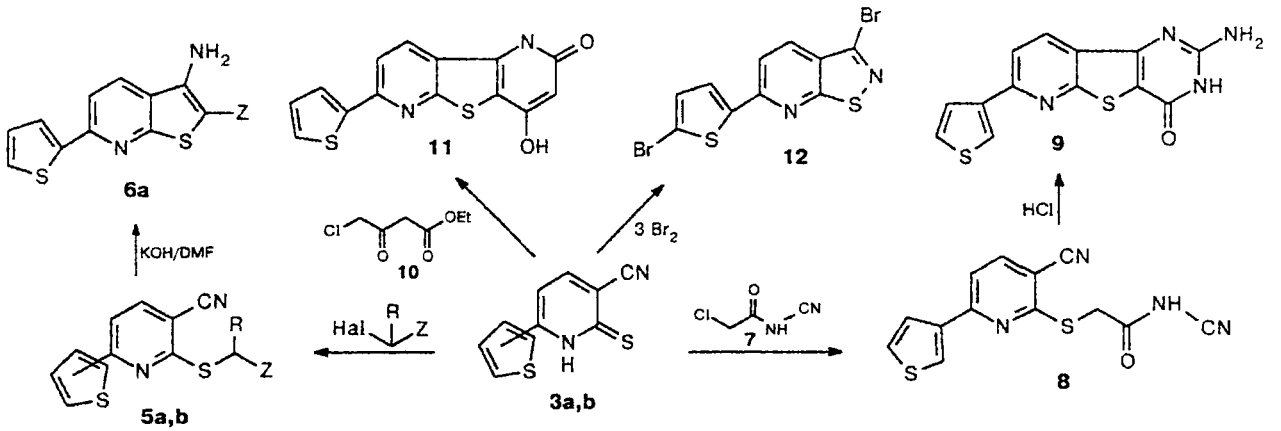
Compounds **3a,b** were used for constructing polyheterocyclic structures. *S*-Alkylation of pyridine derivative **3b** with *N*-cyanochloroacetamide (**7**) in the presence of KOH gave compound **8**, which underwent cyclization into pyridothienopyrimidine (**9**) on treatment with HCl in ethanol. Pyridothienopyridone (**11**) was obtained in one stage by the reaction of compound **3a** with ethyl 4-chloroacetoacetate (**10**) in ethanol in the presence of excess sodium ethoxide.

The bromination of thiopyridone **3a** in chloroform occurs in an unusual way. Irrespective of the amount of bromine, not only closure of the 3-bromoisothiazole ring but also bromination of the thiophene fragment occur to form compound **12**.

Experimental

IR spectra were obtained on a UR-20 instrument (in KBr pellets). ^1H NMR spectra were recorded on a Bruker WM-250 spectrometer in DMSO-d_6. Sodium derivatives of thenoylacetaldehydes **1a,b** were obtained from the corresponding acetylthiophenes and ethyl formate in the presence of sodium ethoxide in dry ether (see Ref. 1). Cyanothioacetamide (**2**) was synthesized by the reaction of malononitrile with hydrogen sulfide according to a reported procedure.[7]

Scheme 2



Z = COOR, COPh CONHPh; Hal = Cl, Br; R = H, Me.

Table 1. Physicochemical and spectroscopic characteristics of alkylthiopyridines **5a,b** and **8**

Thienyl	Z (R)	M.p./°C	Yield (%)	^{1}H NMR, δ (*J*/Hz)	IR, ν/cm^{-1}
3-Thienyl	COOEt (Me)	176—178	86	1.10 (t, 3 H, $\underline{CH_3}CH_2O$, ^3J = 7.5); 1.17 (d, 3 H, $\underline{CH_3}CH$, ^3J = 9.6); 4.15 (q, 2 H, $CH_3\underline{CH_2}O$, ^3J = 7.5); 4.68 (q, 1 H, SCH, ^3J = 9.6; 6.85 (d, 1 H, C(4)H-thiophene, $J_{H(4),H(5)}$ = 3.8); 7.17 (d, 1 H, C(2)H-thiophene, $J_{H(2),H(5)}$ = 1.1); 7.48 (d, 1 H, C(5)H-pyridine, $J_{H(4),H(5)}$ = 8.1); 7.51 (d, 1 H, C(5)H, $J_{H(5),H(4)}$ = 3.8); 7.93 (d, 1 H, C(4)H-pyridine, $J_{H(5),H(4)}$ = 8.1)	2225 (CN); 1720 (CO)
	CONHCN (H)	251—256 (dec.)	67	4.02 (s, 2 H, CH_2); 6.82 (d, 1 H, C(4)H-thiophene, $J_{H(4),H(5)}$ =3.9); 7.20 (d, 1 H, C(2)H-thiophene, $J_{H(2),H(5)}$ = 1.05); 7.45 (d, 1 H, C(5)H-pyridine, $J_{H(4),H(5)}$ = 8.2); 7.48 (dd, 1 H, C(5)H, $J_{H(5),H(4)}$ = 3.9); 7.93 (d, 1 H, C(4)H-pyridine, $J_{H(5),H(4)}$ = 8.1)	3118 (NH), 2221 (Py—CN), 2195 (NH—CN), 1670 (CONH)
2-Thienyl	COPh (H)	152—155	83	4.82 (s, 2 H, S—CH_2); 7.02—8.11 (m, 10 H)	2230 (CN), 1640 (CO)
	COOBu^i (H)	89—92	75	1.12 (d, 6 H, $\underline{CH_3}$—CH); 1.5 (m, 1 H, CH); 4.1 (d, 2 H, O—CH_2); 4.45 (s, 2 H, S—CH_2); 7.17 (t, 1 H, C(4)H-thiophene, $J_{H(4),H(5)}$ = 3.5, $J_{H(4),H(5)}$ = 4.9); 7.24 (d, 1 H, C(5)H, ^3J = 8.1); 7.75 (d, C(3)H-thiophene); 7.82 (d, 1 H, C(5)H-thiophene); 8.15 (d, 1 H, C(4)H, *J* = 8.1)	2225 (CN), 1740 (CO)
	CONHPh	208—210	86	4.5 (2 H, SCH_2); 7.02—8.2 (m, 10 H);	1610 (CO), 2225 (CN), 3290 (NH)

Table 2. Properties of thienylthienopyridines **6a**

Z	M.p./°C	Yield (%)	^{1}H NMR, δ (*J*/Hz)	IR, ν/cm^{-1}
COPh	184—187	86	7.02—8.11 (m)	1610 (CO), 3360 (NH_2)
COOBu^i	120—121	71	1.12 (d, 6 H, $\underline{CH_3}$—CH); 1.1 (m, 1 H, CH); 4.1 (d, 2 H, O—CH_2); 7.05 (br.s, 2 H, NH_2); 7.17 (t, 1 H, C(4)H-thiophene, $J_{H(4),H(5)}$ = 3.5, $J_{H(4),H(5)}$ = 4.9); 7.24 (d, 1 H, C(5)H, ^3J = 8.1); 7.75 (d, 1 H, C(3)H-thiophene); 7.82 (d, 1 H, C(5)H-thiophene); 8.15 (d, 1 H, C(4)H, *J* = 8.1)	1640 (CO), 3280 (NH), 3310 (NH_2), 3420 (NH_2)
CONHPh	252—254	69	7.0—8.55 (m, 12 H); 9.45 (s, 1 H, NH)	1620 (CO), 3290 (NH), 3360 (NH_2), 3460 (NH_2)

Synthesis of pyridine-2(1*H*)-thiones (3a,b) (general procedure). Acetic acid (9 mmol) was added to a suspension of 0.01 mol of the corresponding salt **1a,b** and cyanothioacetamide (0.01 mol) in ethanol (20 mL), and the mixture was heated to 50—60 °C. After stirring for 2 h at 20 °C, AcOH (5 mmol) was added to the reaction mixture, and the resulting precipitate was filtered off and successively washed with water, ethanol, and hexane.

Compounds **3a,b** were used in subsequent reactions without purification; they were recrystallized from acetic acid for analytical purposes.

3-Cyano-6-(2-thienyl)pyridine-2(1*H*)-thione (3a). Yield 60%, m.p. 235—238 °C. Found (%): C, 55.10; H, 2.73; N, 12.75; S, 29.42. $C_{10}H_6N_2S_2$. Calculated (%): C, 55.04; H, 2.75; N, 12.84; S, 29.35. IR, ν/cm^{-1}: 1150 (C=S), 2225 (CN), 3026—3080 (NH). ^{1}H NMR, δ: 7.17 (t, 1 H, C(4)H-thiophene, $J_{H(4),H(3)}$ = 3.5 Hz, $J_{H(4),H(5)}$ = 4.9 Hz); 7.24 (d, 1 H, C(5)H-pyridine, $J_{H(5),H(4)}$ = 7.6 Hz); 7.75 (d, 1 H, C(3)H-thiophene); 7.82 (d, 1 H, C(5)H-thiophene); 8.12 (d, 1 H, C(4)H-pyridine); 13.7 (br.s, 1 H, NH).

3-Cyano-6-(2-thienyl)pyridine-2(1*H*)-thione (3b). Yield 72%, m.p. 244—247 °C (decomp.). Found (%): C, 55.08; H, 2.79; N, 12.87; S, 29.26. $C_{10}H_6N_2S_2$. Calculated (%): C, 55.04; H, 2.75; N, 12.84; S, 29.35. IR, ν/cm^{-1}: 1183 (C=S), 2226 (CN), 3096 (NH). ^{1}H NMR, δ: 6.92 (d, 1 H, C(4)H-thiophene, $J_{H(4),H(5)}$ = 4.8 Hz); 7.22 (s, 1 H, C(2)H-thiophene); 7.28 (d, 1 H, C(5)H-pyridine, $J_{H(5),H(4)}$ = 7.8 Hz); 7.48 (s, 1 H, C(5)H-thiophene); 8.18 (d, 1 H, C(4)H-pyridine); 13.8 (br.s, 1 H, NH).

2-Alkylthiopyridines (5a,b) (general procedure). 10% Aqueous KOH (5.6 mL) and a halocarbonyl compound (0.01 mol) were added successively to 0.01 mol of a suspension of compound **3a** or **3b** in DMF (20 mL), and the reaction mixture was stirred for 3 h at 20 °C. It was then diluted with 5 mL of water, and the precipitate that formed was filtered off and washed with water, ethanol, and hexane. Recrystallization from ethanol gave compounds **5a,b**. Compound **8** was obtained in a similar way.

3-Aminothieno[2,3-*b*]pyridines 6a (general procedure). 10% Aqueous KOH (5.6 mL) was added with stirring to a solution of compound **5a** in DMF obtained by the above procedure, and the mixture was stirred for an additional 5 h at 20 °C. The product was then precipitated by adding water (5 mL), filtered off, and washed with water, ethanol, and hexane. Recrystallization from ethanol gave compounds **6a**.

2-Amino-7-(3-thienyl)-3,4-dihydropyrido[3',2':4,5]thieno[3,2-*b*]pyrimidin-4-one (9). A moderate stream of HCl was passed for 5 min through a suspension of compound **8** (0.5 g) in ethanol (15 mL). The resulting solution was kept for 24 h at 5 °C. The solution was then alkalized with 10 mL of 10% Na_2CO_3, and the precipitate that formed was filtered off and washed with water, ethanol, and hexane. Yield 52%. M.p. >300 °C. IR, ν/cm^{-1}: 1625, 1638 (CONH) 3086, 3156, 3248 (NH, NH_2). ^1H NMR, δ: 6.95 (d, 1 H, C(4)H-thiophene); 7.28 (s, 1 H, C(2)H-thiophene); 7.29 (br.s, 2 H, NH_2), 7.48 (d, 1 H, C(8)H-pyridine, ^3J = 8.2 Hz); 7.53 (d, 1 H, C(5)H-thiophene); 8.32 (d, C(9)H-pyridine, ^3J = 8.2 Hz); 9.04 (br.s, 1 H, NH).

4-Hydroxy-7-(2-thienyl)pyrido[3',2':4,5]thieno[3,2-*b*]pyridin-2(1H)-one (11). Compounds **3a** (0.01 mol) and **10** (0.01 mol) were added in succession with stirring to a solution of EtONa obtained from 0.46 g (0.01 mol) of sodium and 30 mL of ethanol. The reaction mixture was stirred for 1 h at 20 °C and then refluxed for 2 h. After cooling, the reaction mixture was acidified with 2 mL of 10% HCl, and the precipitate was separated and washed with water, ethanol, and hexane. Yield 82%. M.p. >300 °C. IR, ν/cm^{-1}: 1624, 1638 (CONH), 3104 (NH). ^1H NMR, δ: 6.37 (d, 1 H, C(3)H); 7.25 (t, 1 H, C(4)H-thiophene); 7.80 (d,1 H, C(3)H-thiophene); 7.87 (d, 1 H, C(8)H, ^3J = 8.1 Hz); 8.15 (s, 1 H, C(5)-thiophene); 8.16 (d, 1H, C(9)H, ^3J = 8.1 Hz); 10.45 (br.s, 1 H, OH); 11.68 (br.s, 1 H, NH).

3-Bromo-6-(5-bromothienyl-2)-isothiazolo[5,4-*b*]pyridine (12). A mixture of compound **3a** (5 mmol) and bromine (15 mmol) in chloroform (25 mL) was refluxed for 3 h. The solvent was evaporated under reduced pressure, and the residue was recrystallized from nitromethane. Yield 67%. M.p. 248—251 °C. IR, ν/cm^{-1}: 1590, 1604 (C=N). ^1H NMR, δ: 7.41 (d, 1 H, C(3)H-thiophene); 7.42 (d, 1 H, C(4)H-thiophene); 8.12 (d, C(5)H, ^3J = 8.2 Hz); 8.28 (d, 1 H, C(4)H, ^3J = 8.2 Hz).

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Received October 2, 1997

Synthesis of Pd catalysts based on a nonbornene—CO copolymer and their properties in the carbomethoxylation of propylene

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It was found that carboxylation of norbornene (*nbn*) in the presence of the $PdCl_2$—PPh_3—HCl catalytic system is accompanied by alternating copolymerization of *nbn* with carbon monoxide to form norbornanecarboxylic acid (yield ~20%) and a *nbn*-CO copolymer (yield ~80%, M_w = 1600, M_w/M_n = 1.6). The Pd^{II} salt of poly(norbornaneketone)carboxylic acid is a highly active catalyst for the carbomethoxylation of propylene.

Key words: copolymerization, norbornene, carbon monoxide, palladium catalyst, propylene carbomethoxylation.

Metal-containing polymers with controlled distribution of metal atoms in the chain are of considerable interest as catalyst precursors. It is believed that such catalytic systems can possess a number of advantages: enhanced activity and stability, easy regeneration, *etc.*[1] Polymerization of unsaturated compounds catalyzed by

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 2, pp. 368—370, February, 1998.

1066-5285/98/4702-0360 $20.00