ISSN 1070-3632, Russian Journal of General Chemistry, 2011, Vol. 81, No. 1, pp. 160–161. © Pleiades Publishing, Ltd., 2011.
Original Russian Text © V.D. Dyachenko, T.A. Ryl'skaya, 2011, published in Zhurnal Obshchei Khimii, 2011, Vol. 81, No. 1, pp. 162–163.

LETTERS TO THE EDITOR

New Cross Recyclizations of 4-Aryl-2,6-diamino-4*H*-thiopiran-3,5-dicarbonitriles

V. D. Dyachenko and T. A. Ryl'skaya

Taras Shevchenko Lugansk National University, ul. Oboronnaya 2, Lugansk, 91011 Ukraine
e-mail: dvd_lug@online.lg.ua

Received March 11, 2010

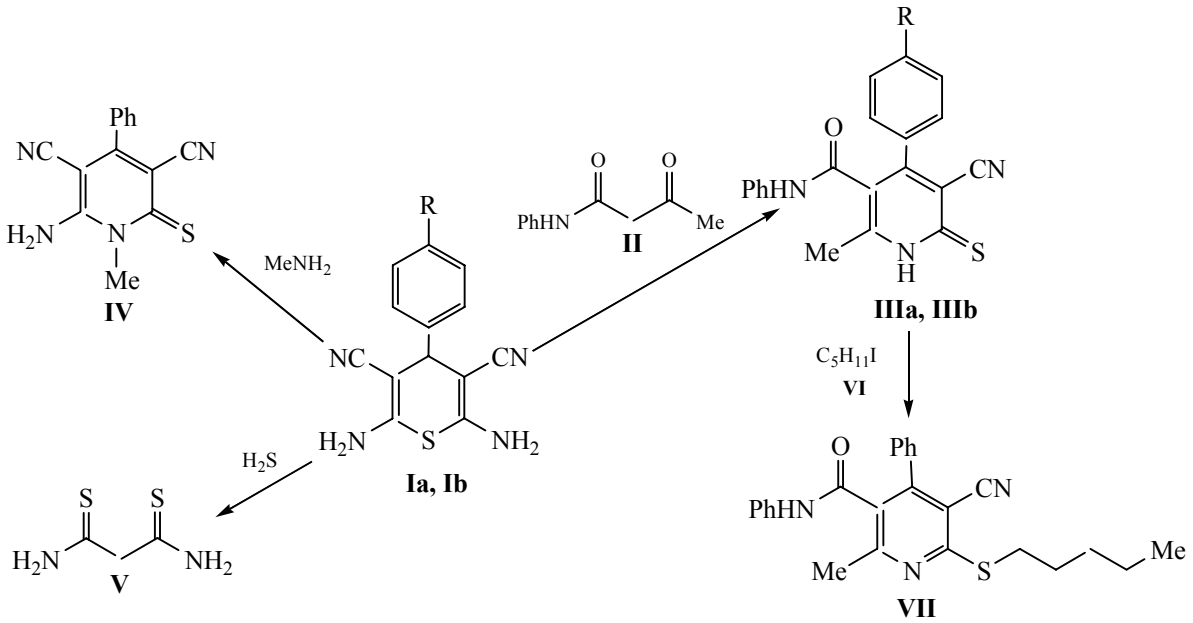
DOI: 10.1134/S1070363211010312

Cross recyclization of 4-aryl-2,6-diamino-4*H*-thiopyran-3,5-dicarbonitriles with acetone leads to the formation of 4-aryl-6-methyl-2-thioxo-1,2-dihydropyridine-3-carbonitriles [1], the reaction with pyridinium ylide gives 5-cyano-3-(1-pyridinio)-1,2,3,4-tetrahydropyridin-6-thiolates [2], and 3-aryl-2-(thiazol-2-yl)acrylonitriles were obtained in reactions with α-bromo carbonyl compounds [3].

We now report for the first time on the cross recyclization of thiopyrans **Ia** and **Ib** with acetoacetanilide (**II**) in boiling ethanol in the presence of *N*-methylmorpholine, which afforded 4-aryl-5-cyano-2-methyl-*N*-phenyl-6-thioxo-1,6-dihydropyridine-3-carboxamides **IIIa** and **IIIb**. By reaction of thiopyran **Ia** with methylamine we obtained 6-amino-1-methyl-4-phenyl-2-thioxo-1,2-dihydropyridine-3,5-dicarbonitrile (**IV**). Treatment of compound **Ia** with hydrogen sulfide in pyridine solution in the presence of triethylamine resulted in the formation of dithiomalonamide **V**. Alkylation of pyridinethione **IIIa** with pentyl iodide (**VI**) gave the corresponding sulfide **VII**. Mechanisms of formation of compounds **III**–**V** and scopes of application of the above reactions are now under study.

Initial thiopyrans **Ia** and **Ib** were synthesized according to the procedure reported in [4].

5-Cyano-2-methyl-*N*,4-diphenyl-6-thioxo-1,6-dihydropyridine-3-carboxamide (IIIa). Three drops of



I, **III**, R = H (**a**), Cl (**b**).

N-methylmorpholine were added to a mixture of 0.51 g (2 mmol) of thiopyran **Ia** and 0.35 g (2 mmol) of acetoacetanilide (**II**) in 10 ml of ethanol, and the mixture was heated for 6 h under reflux. The mixture was cooled to room temperature, treated with 10% hydrochloric acid to pH 2, and left to stand for 48 h. The precipitate was filtered off and washed with ethanol and hexane. Yield 0.32 g (76%), mp 262–264°C (from EtOH); published data [5]: mp 260–262°C. Mass spectrum: *m*/*z* 346 ((I_{rel} 100%) $[M + 1]^+$.

4-(4-Chlorophenyl)-5-cyano-2-methyl-*N*-phenyl-6-thioxo-1,6-dihydropyridine-3-carboxamide (IIIb) was synthesized in a similar way from thiopyran **Ib**. Yield 0.5 g (65%), mp 260–262°C (EtOH). ^{1}H NMR spectrum, δ, ppm: 2.48 s (3H, Me), 7.07 t (1H, H_{arom}, J = 7.5 Hz), 7.27 t (2H, H_{arom}, J = 8.0 Hz), 7.33 d (2H, H_{arom}, J = 8.0 Hz), 7.47 d and 7.55 d (2H each, ClC_6H_4, J = 8.5 Hz), 10.32 s (1H, NHCO), 14.44 br.s (1H, NH). Mass spectrum: *m*/*z* 380 (I_{rel} 100%) $[M + 1]^+$. Found, %: C 63.15; H 3.66; N 10.92. $C_{20}H_{14}ClN_3OS$. Calculated, %: C 63.24; H 3.72; N 11.06.

6-Amino-1-methyl-4-phenyl-2-thioxo-1,2-dihydropyridine-3,5-dicarbonitrile (IV). A mixture of 0.27 g (4 mmol) of methylamine hydrochloride, 0.17 g (2 mmol) of sodium hydrogen carbonate, and 0.51 g (2 mmol) of thiopyran **Ia** in 10 ml of water was heated for 3 h at the boiling point. The mixture was cooled to room temperature, treated with 10% hydrochloric acid to pH 4, and left to stand for 48 h in the cold. The precipitate was filtered off and washed with water, ethanol, and hexane. Yield 0.27 g (54%), mp 285–287°C (from AcOH). ^{1}H NMR spectrum, δ, ppm: 3.96 s (3H, Me), 7.45–7.55 m (5H, Ph), 8.61 br.s (2H, NH_2). Mass spectrum, *m*/*z* (I_{rel}, %): 268 (5) $[M + 2]^+$, 267 (19) $[M + 1]^+$, 266 (100) $[M]^+$, 251 (13) $[M - Me]^+$, 207 (15), 165 (23), 77(21) $[Ph]^+$, 51(14). Found, %: C 63.02; H 3.66; N 20.95. $C_{14}H_{10}N_4S$. Calculated, %: C 63.14; H 3.78; N 21.04.

Propanebis(thioamide) (V). Three drops of triethylamine were added to a mixture of 0.76 g (3 mmol) of thiopyran **Ia** and 20 ml of pyridine, and hydrogen sulfide was bubbled through the mixture over a period of 7 h. The mixture was diluted with a fivefold volume of water and was left to stand in a refrigerator. After 48 h, the precipitate was filtered off and washed with water, ethanol, and hexane. Yield 0.32 g (79%). In analogous reaction with thiopyran **Ib**, the yield of **V** was 0.29 g (70%), mp 135–138°C [6].

5-Cyano-2-methyl-6-pentylsulfanyl-*N*,4-diphenylpyridine-3-carboxamide (VII). Compound **IIIa**, 0.69 g (2 mmol), was dissolved in 10 ml of DMF, 1.12 ml (2 mmol) of 10% aqueous potassium hydroxide and 0.26 ml (2 mmol) of pentyl iodide (**VI**) were added in succession under stirring, and the mixture was stirred for 2 h, diluted with 10 ml of water, and left to stand for 24 h. The precipitate was filtered off and washed with water, ethanol, and hexane. Yield 0.65 g (78%), mp 118–120°C. ^{1}H NMR spectrum, δ, ppm: 0.92 t (3H, Me, J = 6.2 Hz), 1.37–1.48 m (4H, CH_2), 1.74 m (2H, CH_2), 2.62 t (2H, SCH_2, J = 7.2 Hz), 3.34 s (3H, 6-Me), 7.06–7.66 m (10H, Ph), 10.38 br.s (1H, NHCO). Mass spectrum: *m*/*z* 416 (I_{rel} 100%) $[M + 1]^+$. Found, %: C 72.14; H 6.01; N 9.98. $C_{25}H_{25}N_3OS$. Calculated, %: C 72.26; H 6.06; N 10.11.

The ^{1}H NMR spectra were recorded on Bruker DR-500 (500.13 MHz; compounds **IIIa**, **IIIb**, **V**, and **VII**) and Bruker Avance II-400 (400.13 MHz; compound **IV**) spectrometers. The mass spectra (electron impact, 70 eV) were obtained on Kratos MS-890 (**IIIa**, **IIIb**, **V**, **VII**) and MKh-1321 (**IV**) instruments with direct sample admission into the ion source.

REFERENCES

1. Sharanin, Yu.A. and Shestopalov, A.M., *Zh. Org. Khim*., 1989, vol. 25, no. 6, p. 1331.
2. Shestopalov, A.M., Sharanin, Yu.A., and Litvinov, V.P., *Zh. Org. Khim*., 1991, vol. 27, no. 6, p. 1349.
3. Dyachenko, V.D., Chernega, A.N., and Garasevich, S.G., *Russ. J. Gen. Chem*., 2005, vol. 75, no. 10, p. 1610.
4. Sharanin, Yu.A., Shestopalov, A.M., Nesterov, V.N., Melenchuk, S.N., Promanenkov, V.K., Shklover, V.E., Struchkov, Yu.T., and Litvinov, V.P., *Zh. Org. Khim*., 1989, vol. 25, no. 6, p. 1323.
5. Dyachenko, V.D., Krivokolysko, S.G., Nesterov, V.N., and Litvinov, V.P., *Khim. Geterotsikl. Soedin*., 1996, no. 9, p. 1243.
6. Lehr, H., Guex, W., and Erlenmeyer, H., *Helv. Chim. Acta*, 1944, vol. 27, no. 1, p. 970.