ISSN 1070-4280, Russian Journal of Organic Chemistry, 2012, Vol. 48, No. 10, pp. 1386–1387. © Pleiades Publishing, Ltd., 2012.
Original Russian Text © V.D. Dyachenko, 2012, published in Zhurnal Organicheskoi Khimii, 2012, Vol. 48, No. 10, pp. 1389–1390.

## SHORT COMMUNICATIONS

# New Self-transformation of Cyanothioacetamide in the Presence of Bases

**V. D. Dyachenko**

*Taras Shevchenko Lugansk National University, ul. Oboronnaya 2, Lugansk, 91011 Ukraine*
*e-mail: chem@luguniv.edu.ua*

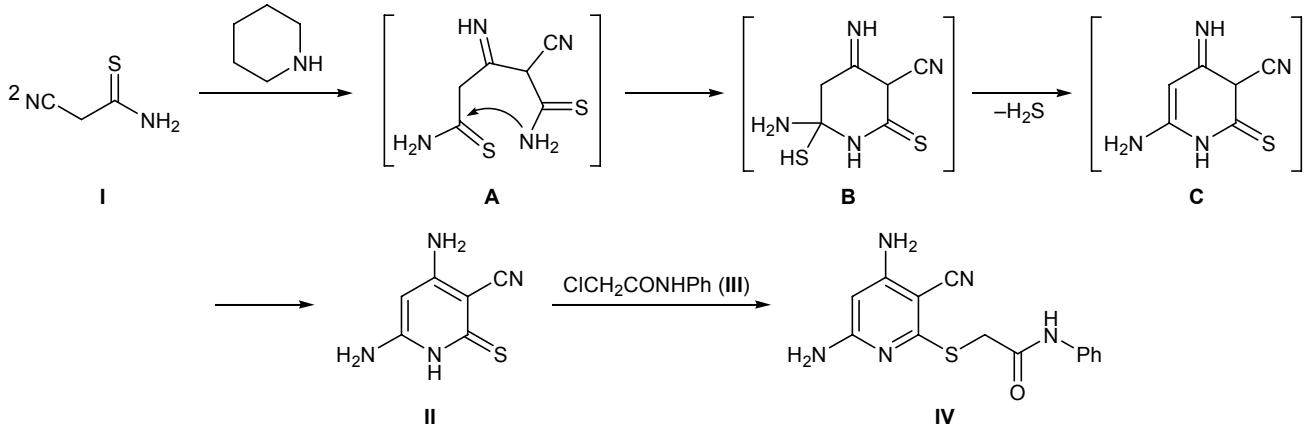
Received April 13, 2012

**DOI:** 10.1134/S1070428012100247

Cyanothioacetamide [1] is used in organic synthesis mostly as CH acid component [2]. On the other hand, two examples of its self-transformation have been reported, namely self-condensation in boiling ethanol in the presence of sodium ethoxide with formation of 4,6-diamino-2-thioxo-2,5-dihydropyridine-3-carbonitrile [3] and Thorpe dimerization [4] to (*E*)-3-amino-2-cyanopent-2-enebis(thioamide) [5].

The present communication describes a new self-transformation of cyanothioacetamide (**I**) in ethanol at 20°C in the presence of an equimolar amount of piperidine, which leads to the formation of 4,6-diamino-2-thioxo-1,2-dihydropyridine-3-carbonitrile (**II**). Compound **II** was synthesized previously by reaction of malononitrile dimer sodium salt with hydrogen sulfide in anhydrous ethanol [6]. When morpholine was used instead of piperidine, other conditions being equal, transamination occurred with formation of 3-(morpholin-4-yl)-3-thioxopropanenitrile, whereas the reaction in the presence of 2 equiv of morpholine involved not only transamination but also intermolecular transfer of hydrogen sulfide to produce 3-(morpholin-4-yl)-3-thioxopropanethioamide [7]. Presumably, compound **II** is formed via initial Thorpe dimerization of **I** to give adduct **A** and its subsequent cyclization to hydrogenated pyridine structure **B** which loses hydrogen sulfide with formation of intermediate **C**. Tautomerization of the latter yields final product **II**. Alkylation of **II** with chloroacetanilide (**III**) in alkaline medium afforded the corresponding sulfide, 2-(4,6-diamino-3-cyanopyridin-3-ylsulfanyl)-*N*-phenylacetamide (**IV**). This reaction is typical of substituted 2-thioxo-1,2-dihydropyridines [8] and 4,6-diamino-2-selenoxo-1,2-dihydropyridine-3-carbonitrile [9] (a selenium-containing analog of **II**).

**4,6-Diamino-2-thioxo-1,2-dihydropyridine-3-carbonitrile (II).** Piperidine, 1 ml (10 mmol), was added under stirring at 20°C to a solution of 1 g (10 mmol) of cyanothioacetamide (**I**) in 20 ml of ethanol, and the mixture was stirred for 4 h and left to stand for 48 h. The precipitate was filtered off and washed with ethanol and hexane. Yield 0.76g (46%), yellow powder, mp 310°C (decomp., from BuOH); sublimes at 250°C; published data [6]: mp 310–312°C. The IR, $^1$H NMR,




I A B C II IV

and mass spectra of **II** were consistent with those given in [6].

**2-(4,6-Diamino-3-cyanopyridin-3-ylsulfanyl)-*N*-phenylacetamide (IV).** Compound **II**, 1.7 g (10 mmol), was dissolved in 15 ml of DMF, 5.6 ml (10 mmol) of 10% aqueous potassium hydroxide and 1.7 g (10 mmol) of chloroacetanilide (**III**) were added in succession under stirring, and the mixture was stirred for 2 h and left to stand for 24 h. The mixture was diluted with an equal volume of water, and the precipitate was filtered off and washed with water, ethanol, and hexane. Yield 2.33 g (78%), brown powder, mp 165–168°C (from BuOH). IR spectrum, ν, $cm^{-1}$: 3398, 3318, 3195 ($NH_2$), 1677 (C=O), 1644 (δNH). $^1H$ NMR spectrum, δ, ppm: 3.95 s (2H, $CH_2$), 5.47 s (1H, 5-H), 6.34 br.s (2H, $NH_2$), 6.45 br.s (2H, $NH_2$), 7.03 t (1H, $H_{arom}$, $J$ = 7.0 Hz), 7.27 t (2H, $H_{arom}$, $J$ = 7.0 Hz), 7.56 d (2H, $H_{arom}$, $J$ = 7.0 Hz), 10.07 br.s (1H, CONH). Mass spectrum: $m/z$ 300 ($I_{rel}$ 100%) $[M + 1]^+$. Found, %: C 56.06; H 4.20; N 23.35. $C_{14}H_{13}N_5OS$. Calculated, %: C 56.17; H 4.38; N 23.40. $M$ 299.357.

The $^1H$ NMR spectra were recorded on a Varian Mercury-400 instrument (400.397 MHz) from solutions in DMSO-$d_6$ using tetramethylsilane as internal reference. The mass spectra were run on a Hewlett Packard 5890/5972 GC–MS system (HP-5MS column; electron impact, 70eV). The elemental compositions were determined on a Perkin–Elmer CHN analyzer. The melting points were determined on a Kofler hot stage. The progress of reactions and the purity of products were monitored by TLC on Silufol UV-254 plates (eluent acetone–hexane, 3 : 5); spots were visualized under UV light or by treatment with iodine vapor.

## REFERENCES

1. Hovard, E.G., US Patent no. 2733260, 1956; *Chem. Abstr*., 1956, vol. 50, p. 12104.
2. Abdel-Galil, F.M., Sherif, Sh.M., and Elnagdi, M.H., *Heterocycles*, 1986, vol. 24, p. 2023; Elnagdi, M.H., Sherif, Sh.M., and Mohareb, R.M., *Heterocycles*, 1987, vol. 26, p. 497; Riad, B.Y., Negm, A.M., Abdou, S.E., and Daboun, H.A., *Heterocycles*, 1987, vol. 26, p. 205; Britsun, V.N., Esipenko, A.N., and Lozinskii, M.O., *Khim. Geterotsikl. Soedin*., 2008, p. 1763.
3. Fahmi, S.M. and Mohareb, R.M., *Tetrahedron*, 1986, vol. 42, p. 687.
4. Vatsuro, K.V. and Mishchenko, G.L., *Imennye reaktsii v organicheskoi khimii* (Name Reactions in Organic Chemistry), Moscow: Khimiya, 1976, p. 398.
5. Mohareb, R.M. and Fahmi, S.M., *Z. Naturforsch., Teil C*, 1986, vol. 41, p. 105.
6. Abu-Shanab, F.A., *J. Chem. Res., Synop*., 1999, p. 430.
7. Dyachenko, V.D., *Russ. J. Gen. Chem*., 2004, vol. 74, p. 641.
8. Dyachenko, V.D. and Litvinov, V.P., *Russ. J. Org. Chem*., 1998, vol. 34, p. 554.
9. Dyachenko, V.D., Sharanin, Yu.A., Litvinov, V.P., Nesterov, V.N., Shklover, V.E., Struchkov, Yu.T., Promonenkov, V.K., and Turov, A.V., *Zh. Obshch. Khim*., 1991, vol. 61, p. 747.