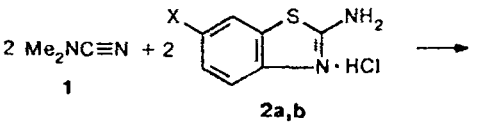
Condensation of 2-aminobenzothiazoles with dimethylcyanamide

V. A. Dorokhov, A. V. Vasilyev, S. V. Baranin, and V. S. Bogdanov*

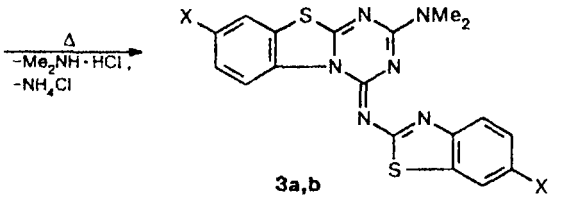
N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences,
47 Leninsky prosp., 117913 Moscow, Russian Federation.
Fax: +7 (095) 135 5328. E-mail: vador@cacr.ioc.ac.ru

The addition of amine hydrochlorides to cyanamides is a standard method for the synthesis of substituted guanidines.[1] It was reported[2] that hydrochlorides of heterocyclic amines can be used in this reaction, and, *e.g.*, heating (180 °C) of 3-amino-1,2-benzoisothiazole hydrochlorides with an excess of dimethylcyanamide (**1**) results in the formation of *N,N*-dimethyl-*N'*-(1,2-benzoisothiazolyl)guanidine.[3]

We have unexpectedly found that the reaction of cyanamide **1** with 2-aminobenzothiazole hydrochlorides (**2a**) (or its 6-bromo-derivative **2b**) under similar conditions is a more complicated process, *viz.*, the condensation of two cyanamide molecules with two molecules of aminoazole hydrochloride (with the elimination of the dimethylamine hydrochloride and NH_4Cl). This results in previously unknown derivatives of 4-(benzothiazol-2-yl)imino-2-dimethylamino-4*H*-1,3,5-triazino-[2,1-*b*]benzothiazole (**3a,b**) isolated in moderate yields.



1 **2a,b**



3a,b

X = H (**a**); Br (**b**)

The structures of compounds **3a,b** were confirmed by the data of IR, ^{1}H NMR, and mass spectra. Their ^{1}H NMR spectra are characterized by the presence of one downfield signal, which can be assigned to the H-6 proton of the triazinobenzothiazole system participating in a weak intramolecular C—H...N (exocycl.) bond.

4-(Benzothiazol-2-yl)imino-2-dimethylamino-4*H*-1,3,5-triazino[2,1-*b*]benzothiazole (3a). A mixture of **2a** (0.195 g, 1.05 mmol) and cyanamide **1** (2 mL, 24.7 mmol) was refluxed for 1 h. The yellow homogeneous solution was cooled to ~20 °C, and acetonitrile (5 mL) was added. The precipitate that formed was filtered off, washed with methanol (3×3 mL), and dried *in vacuo* to give compound **3a** (0.100 g, 50%) with m.p. 250—251 °C (from Me_2NCN). Found (%): C, 56.97; H, 3.93; N, 22.21; S, 16.83. $C_{18}H_{14}N_6S_2$. Calculated (%): C, 57.12; H, 3.73; N, 22.21; S, 16.94. MS, *m/z*: 378 $[M]^+$. IR (KBr), ν/cm^{-1}: 1630, 1580, 1530, 1490 (C=N, C=C). ^{1}H NMR (DMSO-d_6), δ: 9.45 (d); 8.01 (d); 7.88 (d); 7.75 (d); 7.65 (t); 7.55 (t); 7.40 (t); 7.22 (t, 8 H, H arom.); 3.45 and 3.30 (both s, 6 H, NMe_2).

4-(6-Bromobenzothiazol-2-yl)imino-8-bromo-2-dimethylamino-4*H*-1,3,5-triazino[2,1-*b*]benzothiazole (3b) was synthesized similarly from compounds **2b** and **1** in 29% yield, m.p. 355—357 °C (Me_2NCN). Found (%): C, 40.13; H, 2.55; Br, 29.06; N, 15.47; S, 11.62. $C_{18}H_{12}Br_2N_6S_2$. Calculated (%): C, 40.31; H, 2.26; Br, 29.80; N, 15.67; S, 11.96. MS, *m/z*: 536 $[M]^+$. IR (KBr), ν/cm^{-1}: 1630, 1580, 1530, 1490 (C=N, C=C). ^{1}H NMR (DMSO-d_6), δ: 9.25 (d); 8.32 (s); 8.15 (s); 7.64 (d); 7.55 (d); 7.53 (d, 6 H, H arom.); 3.40 and 3.20 (both s, 6 H, NMe_2).

This work was financially supported by the Russian Foundation for Basic Research (Project No. 96-03-32756).

References

1. Houben-Weyl, *Methoden der Organischen Chemie*, Georg Thieme, Stuttgart, 1952, **8**, 180.
2. A. Saxena, R. Aron, S. C. Mehra, and S. K. Tandan, *Ind. J. Pharmacol.*, 1985, **17**, 113 [*Chem. Abstrs.*, 1986, **105**, 164486a].
3. P. Vicini, L. Amoretti, and A. Carretta, *Il Farmaco*, 1992, **47**, 265.

Received April 21, 1998

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 8, pp. 1670—1671, August, 1998.

1066-5285/98/4708-1626 $20.00