Chemistry of Heterocyclic Compounds, Vol. 41, No. 6, 2005

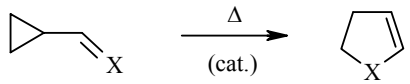
LETTERS TO THE EDITOR

REARRANGEMENT OF 2-AMINO-4-CYCLOPROPYLTHIAZOLIUM BROMIDE

A. V. Samet, S. I. Firgang, and V. V. Semenov

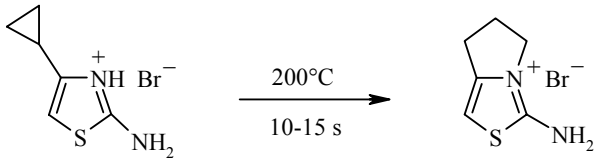
Keywords: 3-amino-6,7-dihydro-5H-pyrrolo[1,2-*c*]thiazolium bromide, 2-amino-4-cyclopropylthiazolium bromide, rearrangement, cyclopropane ring expansion, reaction in the melt.

Cyclopropane ring opening reactions are important for organic synthesis, since they provide a route to obtaining various acyclic and also carbocyclic and heterocyclic compounds [1]. Among these conversions, an important position is occupied by rearrangements of cyclopropanes conjugated with multiple bonds, leading to expansion of the 3-membered ring to form 5-membered carbocycles and heterocycles (cyclopentenes, dihydrofurans, pyrrolines) [2]:



X = C, O, N

Accompanying expansion of the 3-membered ring, we have observed a novel rearrangement of 2-amino-4-cyclopropylthiazolium bromide **1** to 3-amino-6,7-dihydro-5H-pyrrolo[1,2-*c*]thiazolinium bromide **2**:



1 **2** (100%)

This conversion occurs in quantitative yield without a solvent (in the melt, at the melting point of salt **1**) within a few seconds. In addition to its high rate and high yield, note that in this case the cyclopropane ring is not conjugated with the C–N double bond but rather is conjugated with the nitrogen-containing aromatic heterocycle.

The ^{1}H and ^{13}C NMR spectra were taken on a Bruker AM-300 (300 MHz and 75 MHz respectively) in DMSO-d_6, internal standard TMS.

N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, Moscow 119991; e-mail: sametav@yahoo.com. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 6, pp. 914-915, June, 2005. Original article submitted April 8, 2005.

2-Amino-4-cyclopropylthiazolium Bromide (1) was obtained by reaction of bromomethyl cyclopropyl ketone [3] with thiourea in water; mp 197-199°C (H_2O) (melting is accompanied by chemical reaction). ^{1}H NMR spectrum, δ, ppm: 0.7-1.0 (4H, m); 1.9 (1H, m); 6.41 (1H, s, H-5); 9.1 (2H, br. s, NH_2). Found, %: C 32.79; H 3.92; Br 35.75; N 12.80; S 14.61. $C_6H_9BrN_2S$. Calculated, %: C 32.59; H 4.10; Br 36.14; N 12.67; S 14.50. When an aqueous solution of salt **1** is alkalinized, the free base precipitates: **2-amino-4-cyclopropylthiazole (1')**. Mp 79-80°C (H_2O–MeOH). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.72 (4H, d, *J* = 7.7); 1.74 (1H, q, *J* = 7.7); 5.96 (1H, s, H-5); 6.6 (2H, br. s, NH_2). Mass spectrum, *m*/*z* (I_{rel}, %): 140 $[M]^+$ (100), 139 $[M-1]^+$ (81), 97 (80), 81 (90), 80 (51). Found, %: C 51.12; H 5.88; N 20.20; S 23.00. $C_6H_8N_2S$. Calculated, %: C 51.40; H 5.75; N 19.98; S 22.87.

3-Amino-6,7-dihydro-5H-pyrrolo[1,2-*c*]thiazolium Bromide (2). Mp 247-249°C (H_2O). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.58 (2H, m, H-6); 2.80 (2H, t, *J* = 7.5, H-7); 4.00 (2H, t, *J* = 7.5, H-5); 6.59 (1H, s, H-1); 9.4 (2H, br. s, NH_2). ^{13}C NMR spectrum, δ, ppm: 25.3 (C-6); 28.7 (C-7); 48.2 (C-5); 98.2 (C-1); 145.3 (C-7a); 164.4 (C-3). Found, %: C 32.69; H 4.33; Br 35.79; N 12.65; S 14.32. $C_6H_9BrN_2S$. Calculated, %: C 32.59; H 4.10; Br 36.14; N 12.67, S 14.50.

REFERENCES

1. L. A. Yanovskaya, V. A. Dombrovskii, and A. Kh. Khusid, *Cyclopropanes with Functional Groups: Synthesis and Application* [in Russian], Nauka, Moscow (1980).
2. O. G. Kulinkovich, *Usp. Khim.*, **62**, 887 (1993).
3. M. Calverley, *Tetrahedron*, **43**, 4609 (1987).