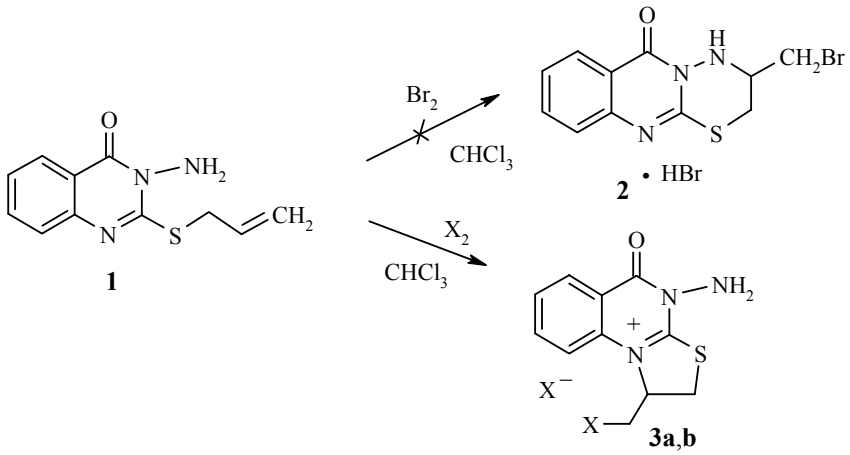
Chemistry of Heterocyclic Compounds, Vol. 41, No. 7, 2005

STRUCTURE OF HALOCYCLIZATION PRODUCTS OF 2-ALLYLSULFANYL-3-AMINO-3,4-DIHYDROQUINAZOLIN-4-ONE

V. N. Britsun, A. N. Esipenko, V. I. Staninets, and M. O. Lozinskii

Keywords: 2-allylsulfanyl-3-amino-3,4-dihydroquinazolin-4-one, 4-amino-1-halomethyl-5-oxo-1,2,4,5-tetrahydro[1,3]thiazolo[3,2-*a*]quinazolin-10-ium halides, halocyclization.

The bromocyclization product of 2-allylsulfanyl-3-amino-3,4-dihydroquinazolin-4-one (**1**) in chloroform is assigned the structure of 3-bromomethyl-2,3-dihydro-4H,6H-[1,3,4]thiadiazino[2,3-*b*]quinazolin-6-one hydrobromide (**2**) in [1]. In the ^{1}H NMR spectrum of the bromocyclization product presented in that paper, there is no signal from the 4-NH amino group since the spectrum was recorded in CF_3COOD. Recently [2] it was shown that halocyclization of azines containing 3-allylsulfanyl and amino groups is accomplished exclusively at the endocyclic nitrogen, which is not consistent with data from the authors of [1].



1 **2** **3a**,**b**

3 a X = Br; X^- = Br^-; **b** X = I, X^- = I_3^-

We have established that halocyclization of compound **1** does not occur at the amino group, as indicated by the authors of [1], but rather occurs at the endocyclic N-1 atom and leads to formation of 4-amino-1-halomethyl-5-oxo-1,2,4,5-tetrahydro[1,3]thiazolo[3,2-*a*]quinazolin-10-ium halides **3a,b**.

In the ^{1}NMR spectra of compounds **3a,b**, typical features are signals from protons of the NH_2 group and the 1-CH, 2-CH_2 protons of the thiazole ring (respectively 6.68-6.70 ppm, 6.06-6.26 ppm, and 3.77-4.10 ppm). In the IR spectra of **3a,b**, we observe characteristic absorption bands for the NH_2 and C=O groups (3300 cm^{-1} and 1720-1730 cm^{-1}). The ^{13}C NMR spectrum of the triiodide **3b** also suggests formation of a thiazole ring,

Institute of Organic Chemistry, National Academy of Sciences of Ukraine, Kiev 02094; e-mail: esipenko@iflab.kiev.ua. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 7, pp. 1114-1115, July, 2005. Original article submitted April 28, 2005.

since the signal from the C-1 atom (66.6 ppm) appears as a doublet (J = 152 Hz) in the ^{13}C NMR spectrum recorded without spin–spin decoupling. The composition of the synthesized compounds **3a,b** is confirmed by elemental analysis.

The ^{1}H NMR spectra were recorded (300 MHz) in DMSO-d_6, internal standard TMS.

4-Amino-1-bromomethyl-5-oxo-1,2,4,5-tetrahydro[1,3]thiazolo[3,2-*a*]quinazolin-10-ium Bromide (3a). A solution of bromine (0.158 g, 1 mmol) in chloroform (3 ml) was added dropwise to a solution of quinazolin-4-one **1** (0.233 g, 1 mmol) in chloroform (5 ml) at 0°C. The solution was held for 0.5 h and the salt **3a** was filtered out. Yield 0.267 g (68%); mp 268-270°C (benzonitrile). IR spectrum (KBr), ν, cm^{-1}: 3300 (NH_2), 3100-2950, 1730 (C=O), 1640 (C=N), 1620, 1550, 1490, 1470, 1440. ^{1}H NMR spectrum, δ, ppm (J, Hz): 3.79 (1H, m, CH_2Br); 3.97 (1H, m, CH_2Br); 4.10 (2H, m, 2-CH_2); 6.26 (1H, m, 1-CH); 6.70 (2H, s, NH_2); 7.76 (1H, m, H_{Ar}); 7.98 (1H, d, J = 8.1, H_{Ar}); 8.10 (1H, m, H_{Ar}); 8.30 (1H, d, J = 8.4, H_{Ar}). Found, %: C 33.37; H 3.10; N 10.82. $C_{11}H_{11}Br_2N_3OS$. Calculated, %: C 33.61; H 2.82; N 10.69.

4-Amino-1-iodomethyl-5-oxo-1,2,4,5-tetrahydro[1,3-thiazolo[3,2-*a*]quinazolin-10-ium Triiodide (3b) was obtained as for compound **3a**. Yield 82%; mp 210-212°C (nitromethane). IR spectrum (KBr), ν, cm^{-1}: 3300 (NH_2), 3000, 1720 (C=O), 1640 (C=N), 1630, 1550, 1490, 1440. ^{1}H NMR spectrum, δ, ppm (J, Hz): 3.63 (1H, m, CH_2I); 3.73 (1H, m, CH_2I); 3.77 (1H, m, 2-CH_2); 4.10 (1H, m, 2-CH_2); 6.06 (1H, m, 1-CH); 6.68 (2H, s, NH_2); 7.76 (1H, m, H_{Ar}); 7.89 (1H, d, J = 8.1, H_{Ar}); 8.08 (1H, m, H_{Ar}); 8.30 (1H, d, J = 7.5, H_{Ar}). ^{13}C NMR spectrum (75 MHz, DMSO-d_6), δ, ppm: 3.4 (CH_2I), 34.3 (C-2), 66.6 (C-1), 117.2 (C_{Ar}), 117.7 (C_{Ar}), 128.4 (C_{Ar}), 128.5 (C_{Ar}), 135.9 (C_{Ar}), 137.0 (C_{Ar}), 157.9 (C=S), 172.8 (C=O). Found, %: C 18.05; H 1.38; N 5.88. $C_{11}H_{11}I_4N_3OS$. Calculated, %: C 17.83; H 1.50; N 5.67.

REFERENCES

1. H. K. Gakhar, S. Kiran, and S. B. Gupta, *Monatsh. Chem.*, **113**, 1145 (1982).
2. N. Yu. Slivka and Yu. I. Gevaza, *Ukr. Khim. Zh.*, **68**, No. 12, 89 (2002).