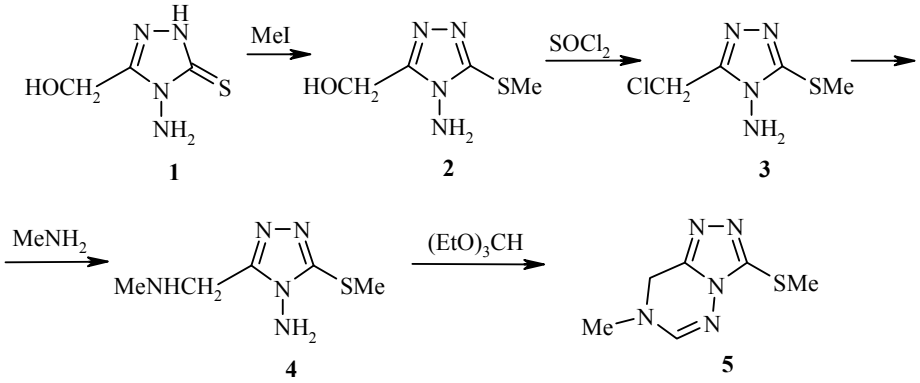
Chemistry of Heterocyclic Compounds, Vol. 40, No. 1, 2004

SYNTHESIS OF A NOVEL HETEROCYCLIC SYSTEM: 7-METHYL-3-METHYLTHIO-7,8-DIHYDRO[1,2,4]TRIAZOLO[3,4-*f*][1,2,4]TRIAZINE

L. Labanauskas, V. Bucinskaite, D. Bucyte, A. Brukstus

Keywords: 7,8-dihydro[1,2,4]triazolo[3,4-*f*][1,2,4]triazine, 4-amino-3-chloromethyl-5-methylthio-4H-1,2,4-triazole, 4-amino-3-methylaminomethyl-5-methylthio-4H-1,2,4-triazole, condensation.

During a study of triazoles and related condensed heterocycles [1], we synthesized 7-methyl-3-methylthio-7,8-dihydro[1,2,4]triazolo[3,4-*f*][1,2,4]triazine (**5**), which is a previously unknown heterocyclic system. The amino alcohol **2** obtained by methylation of thione **1** is converted to the chlorinated derivative **3**, and then to the methylamino derivative **4**. Compound **5** is obtained by condensation of the latter with ethyl orthoformate. In its IR spectrum, there were no vibrational bands for the amino groups, but in the ^{1}H NMR spectrum we observed a signal from the methine proton at 7.11 ppm.



The IR spectra were obtained on an FT-IR Spectrum BX II (Perkin-Elmer) spectrophotometer in nujol, while the NMR spectra were obtained on a Tesla BS-587A (80 MHz) in DMSO-d_6, internal standard TMS.

4-Amino-5-methylthio-4H-1,2,4-triazol-3-ylmethanol (2). Sodium (0.5 g, 22 mmol) and then thione **1** (3 g, 21 mmol) [1] and iodomethane (1.3 ml, 22 mmol) were dissolved in methanol (50 ml). The mixture was boiled for 1.5 h, neutralized with acetic acid, and evaporated to dryness. The residue was triturated with hot toluene (20 ml), the toluene was decanted off and then it was cooled. The precipitate was recrystallized from 2-propanol and we obtained 1.2 g (37%) of compound **2**; mp 135-138°C. IR spectrum, ν, cm^{-1}: 3378, 3290 (NH_2), 3083 (OH). ^{1}H NMR spectrum, δ, ppm: 2.58 (3H, s, SCH_3); 4.56 (2H, s, CH_2); 5.42 (1H, s, OH); 5.86 (2H, s, NH_2). Found, %: C 30.28; H 4.91; N 34.88. $C_4H_8N_4OS$. Calculated, %: C 29.99; H 5.03; N 34.97.

Vilnius University, Organic Chemistry Department, Vilnius 2006, Lithuania; e-mail: linas.labanauskas@chf.vu.lt. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 1, pp. 130-131, January, 2004. Original article submitted October 13, 2003.

4-Amino-3-chloromethyl-5-methylthio-4H-1,2,4-triazole (3). A solution of compound **2** (0.15 g, 0.94 mmol) in thionyl chloride (10 ml) was held for 30 min at 20°C and evaporated down under vacuum without heating. The dry residue was recrystallized from 2-propanol and we obtained 0.1 g (60%) of compound **3**; mp 130-133°C. IR spectrum, ν, cm^{-1}: 3303, 3126 (NH_2). ^1H NMR spectrum, δ, ppm: 2.68 (3H, s, SCH_3); 4.82 (2H, s, CH_2); 7.88 (2H, br. s, NH_2). Found, %: C 26.48; H 4.21; N 31.58. $C_4H_7ClN_4S$. Calculated, %: C 26.89; H 3.95; N 31.36.

4-Amino-3-methylaminomethyl-5-methylthio-4H-1,2,4-triazole (4). A solution of 4-amino-3-chloromethyl-5-methylthio-4H-1,2,4-triazole **3** (0.8 g, 4.5 mmol) and methylamine (0.42 g, 13.5 mmol) in methanol (30 ml) was boiled for 1.5 h; the solvent was evaporated off under vacuum, and a crude oily product **4** was obtained. A chloroform solution of compound **4** was washed with water. IR spectrum, ν, cm^{-1}: 3365, 3318, 3220 (NH, NH_2). ^1H NMR spectrum, δ, ppm: 2.70 (3H, s, SCH_3); 3.98 (2H, s, CH_2); 4.22 (2H, s, NH_2).

7-Methyl-3-methylthio-7,8-dihydro[1,2,4]triazolo[3,4-*f*][1,2,4]triazine (5). Unpurified compound **4** from the previous reaction and ethyl orthoformate (5 ml) were heated for 1 h at a temperature of 130°C, cooled down, filtered, and recrystallized from 2-propanol. Obtained 0.75 g (75% relative to compound **3**) of compound **5**; mp 234-235°C. ^1H NMR spectrum, δ, ppm: 2.67 (3H, s, SCH_3); 3.08 (3H, s, NCH_3); 4.66 (2H, s, CH_2); 7.11 (1H, s, CH). Found, %: C 39.28; H 5.26; N 38.35. $C_6H_9N_5S$. Calculated, %: C 39.33; H 4.95; N 38.22.

REFERENCES

1. L. Labanauskas, V. Buchinskaite, V. Bucinskaite, A. Brukstus, and G. Urbalis, *Khim. Geterotsikl. Soedin.*, 948 (2003).
2. W. L. Albrecht and D. W. Jones, US Patent 4230715; *Chem. Abstr.* **94**:121552f (1981).