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SYNTHESIS OF A NOVEL HETEROCYCLIC SYSTEM: 2H-2,3,5,6,9-PENTAAZABENZ[*cd*]AZULENE

S. Tumkevicius and Z. Sarakauskaite

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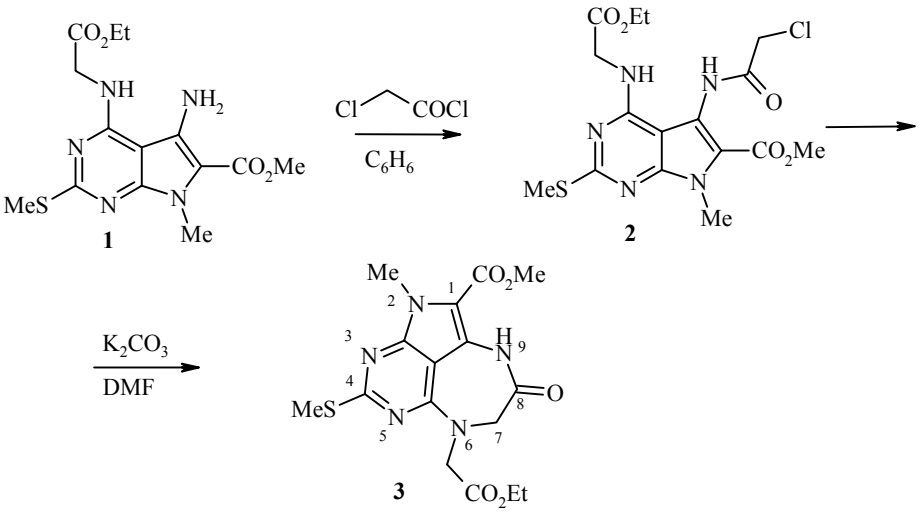
Continuing our studies in the area of condensed pyrimidine heterocycles [1-3], we have developed a simple and convenient method for synthesis of the first representative of a novel heterocyclic system: the methyl ester of 6-(ethoxycarbonylmethyl)-2-methyl-4-methylthio-8-oxo-6,7,8,9-tetrahydro-2H-2,3,5,6,9-pentaazabenz-[*cd*]azulene-1-carboxylic acid (**3**).

The diazepine ring, *peri*-condensed with a pyrrolo[2,3-*d*]pyrimidine moiety, was obtained by acylation of the primary amino group of compound **1** with chloroacetyl chloride followed by intramolecular cyclocondensation of the 5-chloroacetylamino derivative of pyrrolo[2,3-*d*]pyrimidine **2** formed, in the presence of potassium carbonate in DMF. Compound **1** was synthesized by a three-step method from 4,6-dichloro-2-methylthiopyrimidine-5-carbonitrile, which will be described in a separate paper.

The IR spectra were obtained on a Spectrum BX II FT-IR spectrophotometer (Perkin-Elmer) in vaseline oil; the ^{1}H NMR spectra were obtained on a Tesla BS-587A (80 MHz) in $CDCl_3$, internal standard TMS.



Methyl Ester of 5-Chloroacetylamino-4-(ethoxycarbonyl)methylamino-7-methyl-2-methylthio-7H-pyrrolo[2,3-*d*]pyrimidine-6-carboxylic Acid (2). Chloroacetyl chloride (0.21 g, 1.85 mmol) was added dropwise, with stirring at room temperature, to a mixture of compound **1** (0.5 g, 1.41 mmol) in anhydrous benzene (20 ml). The reaction mixture was refluxed for 15 min and then cooled down to room temperature; the

Department of Organic Chemistry, Vilnius University, Vilnius 2006, Lithuania; e-mail: sigitas.tumkevicius@chf.vu.lt. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 12, pp. 1731-1732, December, 2002. Original article submitted November 15, 2002.

precipitate was filtered out and recrystallized. Obtained 0.5 g (82%) of compound **2**; mp 205-206°C (ethanol). IR spectrum, ν, cm^{-1}: 3326, 3286 (NH); 1740, 1714, 1706 (CO). ^{1}H NMR spectrum, δ, ppm, *J* (Hz): 1.30 (3H, t, *J* = 7, CH_3); 2.57 (3H, s, SCH_3); 3.94 (3H, s, NCH_3); 3.98 (3H, s, OCH_3); 4.28 (2H, q, *J* = 6, OCH_2); 4.33 (2H, d, *J* = 5, NCH_2); 4.35 (2H, s, CH_2Cl); 7.49 (1H, br. t, *J* = 5, NH); 10.20 (1H, s, NHCO). Found, %: C 44.96; H 4.93; N 15.98. $C_{16}H_{20}ClN_5O_5S$. Calculated, %: C 44.70; H 4.69; N 16.29.

Methyl Ester of 6-(Ethoxycarbonyl)methyl-2-methyl-4-methylthio-8-oxo-6,7,8,9-tetrahydro-2H-2,3,5,6,9-pentaazabenz[*cd*]azulene-1-carboxylic Acid (3). Anhydrous potassium carbonate (0.065 g, 0.47 mmol) was added to a solution of compound **2** (0.2 g, 0.47 mmol) in anhydrous DMF (10 ml). The reaction mixture was stirred at 50-60°C for 7 h. After cooling down to room temperature, the precipitate was filtered out, water was added to the filtrate, the precipitate was filtered out and combined with the previously obtained precipitate, and recrystallized. Obtained 0.17 g (91%) of compound **3**; mp 209-210°C (ethanol–dioxane). IR spectrum, ν, cm^{-1}: 3395 (NH); 1740, 1710, 1683 (CO). ^{1}H NMR spectrum, δ, ppm, *J* (Hz): 1.28 (3H, t, *J* = 7, CH_3); 2.54 (3H, s, SCH_3); 3.93 (3H, s, NCH_3); 3.96 (3H, s, OCH_3); 4.26 (2H, q, *J* = 7, OCH_2); 4.30 (2H, s, NCH_2CO); 4.42 (2H, s, CH_2CO_2Et); 9.09 (1H, s, NH). Found, %: C 49.06; H 4.89; N 17.65. $C_{16}H_{19}N_5O_5S$. Calculated, %: C 48.85; H 4.87; N 17.80.

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