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SYNTHESIS OF DERIVATIVES OF A NEW HETEROCYCLIC SYSTEMS – 7-THIA-5,8,11-TRIAZAINDENO[1,2-*c*]FLUORENE

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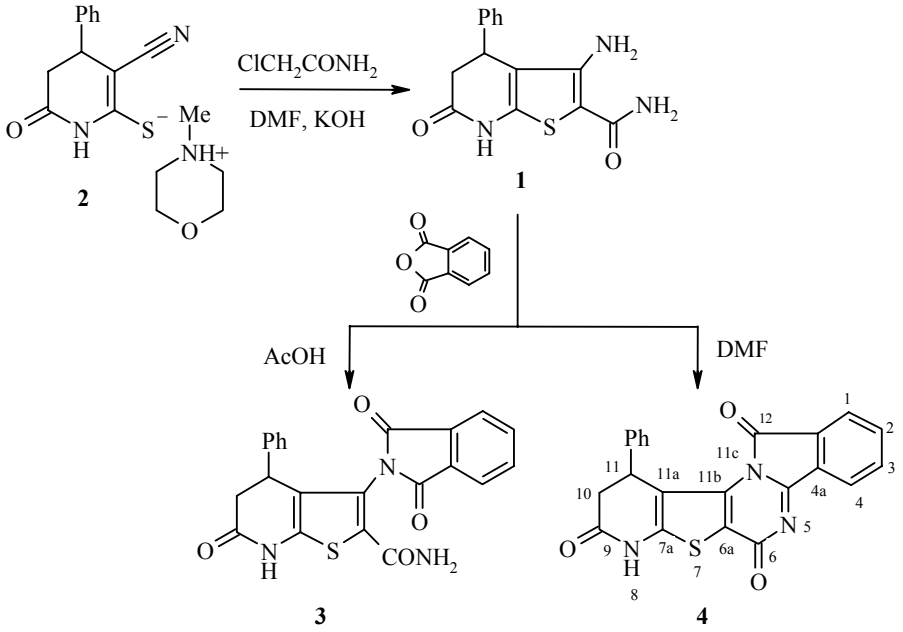
Interest in the chemistry of derivatives of thieno[2,3-*b*]pyridine is linked, in the first place, to their accessibility, and also to the broad potential of the practical use of compounds of this class [1]. In a continuation of our investigations in the field of synthesis of condensed thienopyridines [2] we decided to study the possibility of polycyclic products under conditions of cyclocondensation of phthalic anhydride with thieno[2,3-*b*]pyridine **1**, which is readily prepared from the thiolate **2** and α-chloroacetamide under Thorpe-Ziegler conditions [3]. It was established that in boiling AcOH the reaction stopped at the stage of the formation of the 3-phthalimido derivative **3** in 81% yield, whereas in boiling DMF a deeper condensation occurred to give a derivative of a new heterocyclic system – 7-thia-5,8,11c-triazindeno[1,2-*c*]fluorene **4**.



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Evidently the temperature and the low solubility of compound **3** in AcOH have an important influence on the course of the condensation process.

^{1}H NMR spectra of DMSO-d_6 solutions with TMS as internal standard were recorded with a Varian Gemini 200 (200 MHz) instrument. IR spectra of nujol mulls were recorded with an IKC-29 spectrophotometer. Elemental analyses were carried out with a Perkin-Elmer CHN analyzer. The thiolate **2** was prepared by a known method [4].

3-Amino-6-oxo-4-phenyl-4,5,6,7-tetrahydrothieno[2,3-*b*]pyridine-2-carboxamide (1) was obtained by a modified procedure [3]: 10% KOH (15.7 ml, 30 mmol) was added to a solution of thiolate **2** (10 g, 30 mmol) in DMF (30 ml), and stirred with heating until solution was complete. The mixture was filtered to α-chloroacetamide (3.0 g, 32 mmol) in DMF (5 ml), heated to boiling, stirred at ~50°C for 3 h, kept over night, then more 10% KOH (15.7 ml) was added, boiled for 5 min, kept for 2 d, and then diluted with water (200 ml). The precipitate which formed over 7 d was filtered off and washed with water. Yield 80%; mp 258-260°C (from 3:1 EtOH–AcOH). IR spectrum, ν, cm^{-1}: 1677, 1644 (2C=O) 3165, 3305, 3455, 3483 (NH, 2 NH_2). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 10.65 (1H, s, NH); 7.29-7.13 (5H, m C_6H_5); 6.44 (2H, br. s, $CONH_2$); 6.32 (2H, br. s, NH_2); 4.27 (1H, br. pseudo d, H-4); 3.10 (1H, dd, ^2J = 16.2, ^3J = 7.6, H-5); 2.64 (1H, br. pseudo d, ^2J = 16.2, H-5). Found, %: C 58.98; H 4.58; N 14.58. $C_{14}H_{13}N_3O_2S$. Calculated, %: C 58.52; H 4.56; N 14.62.

6-Oxo-4-phenyl-3-phthalimido-4,5,6,7-tetrahydrothieno[2,3-*b*]pyridine-2-caroxamide (3). A mixture of thienopyridine **1** (1.3 g, 3.5 mmol) and phthalic anhydride (1.3 g, 8.8 mmol) in AcOH (15 ml) was boiled with stirring for 4 h, kept for 24 h at ~20°C, the precipitate was filtered off, and washed with hot EtOH to give pure thienopyridine **3** as white crystals (1.18 g, 81), mp 350-355°C (dec). IR spectrum, ν, cm^{-1}: broad absorption band 1724-1643 (4C=O), 3150, 3373 (NH, NH_2). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 10.96 (1H, s, NH); 7.79-7.65 (4H, m, $Ar_{phthalimid}$); 7.28 (2H, br. s, $CONH_2$); 697-6.80 (5H, m, C_6H_5); 4.09 (1H, br. pseudo d, H-4); 2.85-2.63 (2H, m, H-5). Found, %: C 63.66; H 3.63; N 10.03. $C_{22}H_{15}N_3O_4S$. Calculated, %: C 63.30; H 3.62; N 10.07.

6,9,12-trioxo-11-phenyl-8,9,10,11-tetrahydro-6H,12H-7-thia5.8.11c-triazaindeno[1,2-*c*]fluorine 4. A mixture of thienopyridine **1** (1 g, 3.5 mmol) and phthalic anhydride (1.3 g, 8.8 mmol) in DMF (13 ml) was boiled for 10 h, kept for 24 h at ~20°C, the bright yellow product was filtered off and washed with hot EtOH. Yield 0.74 g (53%); mp >350°C (from DMF). IR spectrum, ν, cm^{-1}: 1773, 1696, 1677 (3C=O, C=N). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 11.25 (1H, s, NH); 7.97-7.77 (4H, m, $Ar_{phthalimid}$); 7.37-7.21 (5H, m, C_6H_5); 4.66 (1H, br. pseudo d, H-4); 3.25-2.63 (2H, m, overlapping signals, H-5). Found, %: C 65.41; H 3.30; N 10.62. $C_{22}H_{15}N_3O_3S$. Calculated, %: C 66.16; H 3.28; N 10.52.

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