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THE FORMATION OF THE PYRIDINE RING IN THE SYNTHESIS OF DIPYRIDO-[3',2':4,5]THIENO[3,2-*b*:3,2-*d*]PYRIDINES

V. K. Vasilin[1], M. M. Lipunov[1], L. D. Konyushkin[2], E. A. Kaigorodova[1], and G. D. Krapivin[1]

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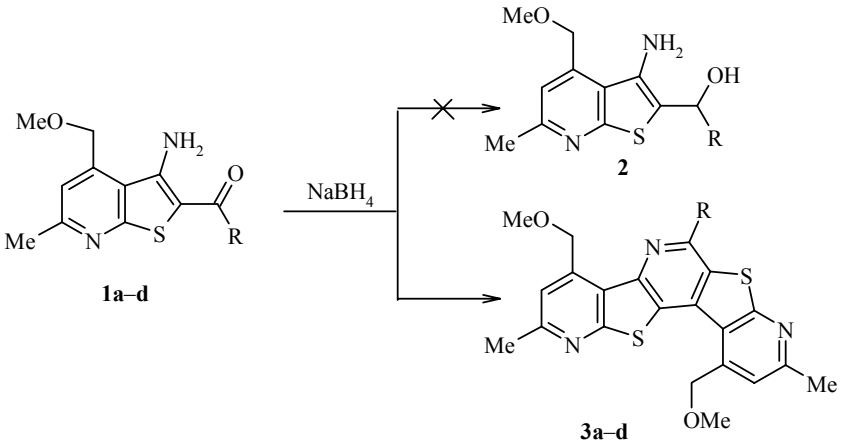
While continuing our investigations into the reactivity of substituted 3-aminothieno[2,3-*b*]pyridines [1, 2], we found a new reaction leading to closure of the pyridine ring during the formation of a pentacyclic heteroaromatic 22π-electronic system dipyridothienopyridine.

During an attempt to reduce the carbonyl group of compounds **1a-d** with sodium borohydride in ethanol the corresponding dipyrido[3',2':4,5]thieno[3,2-*b*:3,2-*d*]pyridines **3a-d** were isolated from the reaction mixture instead of the expected amino alcohols **2**. The mechanism of the transformations that occur is not quite clear and will be the subject of further investigations.



1a–d

1, **3 a** R = Ph; **b** R = C_6H_4Br-4; **c** R = $C_6H_3Cl_2$-2,4; **d** R = Me

The ^{1}H NMR spectra were recorded in trifluoroacetic acid (compounds **3a-c**) and DMSO-d_6 (compound **3d**) on a Bruker DRX-500 instrument (500 MHz).

Synthesis (General Procedure). Compound **1** (0.005 mol) was dissolved by heating in ethanol (20 ml), and sodium borohydride (7.5 mmol) was added while the reaction mixture was stirred. The obtained solution was boiled for 3 h, cooled, and neutralized with a 10% solution of hydrochloric acid. The flocculent precipitate was separated and washed with boiling DMF, water, and ethanol. The products were recrystallized from ethanol.

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[1] Kuban State Technological University, Krasnodar, Russia; e-mail: organics@kubstu.ru. [2] N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, Moscow; e-mail: Leonid@chemical-block.com. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 10, pp. 1582-1583, 2006. Original article submitted June 30, 2005. Revision submitted February 28, 2006.

4,9-di(methoxymethyl)-6,11-Dimethyl-2-phenyldipyrido[3',2':4,5]thieno[3,2-*b*:3,2-*d*]pyridine (3a). Yield 23%; mp >350°C. ^{1}H NMR spectrum, δ, ppm: 3.15 (6H, s, CH_3); 4.01 (6H, s, OCH_3); 6.11 (4H, s, OCH_2); 7.80-7.90 (5H, m, H_{Ph}); 8.36 (2H, s, H_{Py}). Mass spectrum (EI, 70 eV), *m*/*z* (I_{rel}, %): 485 $[M]^+$ (30), 470 $[M - CH_3]^+$ (72), 438 $[M - CH_3 - CH_3OH]^+$ (31), 410 $[M - CH_3 - CH_3OH - CO]^+$ (63), 369 $[M - CH_3 - CH_3OH - CO - C_3H_5]^+$ (16), 205 $[M - C_{17}H_{14}NOS]^+$ (100). Found, %: C 66.85; H 4.73; N 8.62. $C_{27}H_{23}N_3O_2S_2$. Calculated, %: C 66.78; H 4.77; N 8.65.

2-(4-Bromophenyl)-4,9-di(methoxymethyl)-6,11-dimethyldipyrido[3',2':4,5]thieno[3,2-*b*:3,2-*d*]-pyridine (3b). Yield 27%; mp 316-317°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.97 (6H, s, CH_3); 3.84 (6H, s, OCH_3); 5.97 (4H, s, OCH_2); 7.53 (2H, d, *J* = 8.0, 3,5-H_{Ar}); 7.78 (2H, d, *J* = 8.0, 2,6-H_{Ar}); 8.18 (2H, s, H_{Py}). Mass spectrum* (EI, 70 eV), *m*/*z* (I_{rel}, %): 548 $[M - CH_3]^+$ (9), 488 $[M - CH_3 - CH_3OH - CO]^+$ (6), 44 $[CS]^+$ (100). Found, %: C 57.50; H 3.90; N 7.41. $C_{27}H_{22}BrN_3O_2S_2$. Calculated, %: C 57.45; H 3.93; N 7.44.

2-(2,4-Dichlorophenyl)-4,9-di(methoxymethyl)-6,11-dimethyldipyrido[3',2':4,5]thieno[3,2-*b*:3,2-*d*]-pyridine (3c). Yield 26%; mp >350°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.71 (6H, s, CH_3); 3.68 (6H, s, OCH_3); 5.62 (4H, s, OCH_2); 7.64-7.76 (3H, m, H_{Ar}); 7.96 (2H, s, H_{Py}). Mass spectrum*[2] (EI, 70 eV), *m*/*z* (I_{rel}, %): 553 $[M]^+$ (28), 538 $[M-CH_3]^+$ (100), 506 $[M - CH_3 - CH_3OH]^+$ (41), 478 $[M - CH_3 - CH_3OH - CO]^+$ (88), 423 $[M - CH_3 - CH_3OH - CO - C_4H_7]^+$ (10), 408 $[M - CH_3 - CH_3OH - CO - C_4H_7 - CH_3]^+$ (32). Found, %: C 58.57; H 3.79; N 7.54. $C_{27}H_{21}Cl_2N_3O_2S_2$. Calculated, %: C 58.48; H 3.82; N 7.58.

4,9-Di(methoxymethyl)-2,6,11-trimethyldipyrido[3',2':4,5]thieno[3,2-*b*:3,2-*d*]pyridine (3d). Yield 23%; mp 305-306°C. ^{1}H NMR spectrum, δ, ppm: 2.71 (6H, s, CH_3); 2.83 (3H, s, CH_3); 3.65 (6H, s, OCH_3); 5.56 (4H, s, OCH_2); 7.61 (2H, s, H_{Py}). Found, %: C 62.30; H 5.01; N 9.88. $C_{22}H_{21}N_3O_2S_2$. Calculated, %: C 62.39; H 5.00; N 9.92.

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* The isotopic peaks for ^{79}Br are given.

*[2] The isotopic peaks for ^{35}Cl are given.