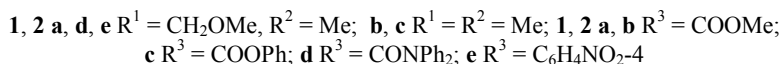
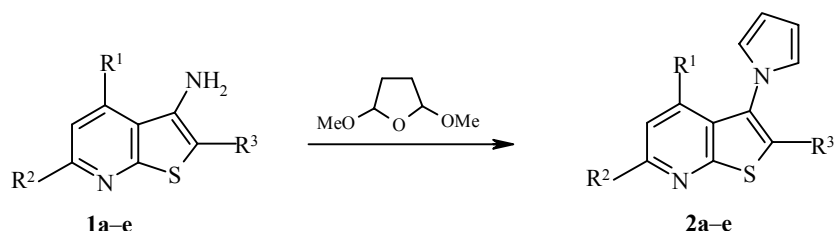


3-(1-PYRROLYL)THIENO[2,3-*b*]PYRIDINE – A NEW CONJUGATED HETEROCYCLIC SYSTEM

E. A. Kaigorodova, A. A. Osipova, V. K. Vasilin, L. D. Konyushkin, and G. D. Krapivin

Keywords: 3-aminothieno[2,3-*b*]pyridine, 3-(1-pyrrolyl)thieno[2,3-*b*]pyridine.

In a continuation of work on the synthesis of conjugated heterocyclic systems from 3-aminothieno[2,3-*b*]pyridine [1-3], we obtained a new heterocyclic system, namely, 3-(1-pyrrolyl)thieno[2,3-*b*]pyridine **2a-c**, by the reactions of **1a-c** with 2,5-dimethoxytetrahydrofuran.



Methyl 4-Methoxymethyl-6-methyl-3-(1-pyrrolyl)thieno[2,3-*b*]pyridine-2-carboxylate (2a). A solution of methyl 3-amino-4-methoxymethyl-6-methylthieno[2,3-*b*]pyridine-2-carboxylate (**1a**) (1 g, 3.75 mmol) in glacial acetic acid (4 ml) was heated to reflux and, then, 2,5-dimethoxytetrahydrofuran (0.58 ml, 4.48 mmol) was added with stirring. The reaction mixture was heated at reflux for 3 h, cooled, and then diluted with ice water (15 ml). The precipitate formed was separated, washed until the wash water was neutral, and dried in the air. The product was recrystallized from ethanol to give 1.25 g (91%) **2a**; mp 119-120°C. ¹H NMR spectrum (DMSO-*d*₆, 200 MHz), δ, ppm: 2.65 (3H, s, CH₃); 3.21 (3H, s, OCH₃); 3.73 (3H, s, CO₂CH₃); 3.93 (2H, s, OCH₂); 6.27 (2H, s, H_β); 6.73 (2H, s, H_α); 7.37 (1H, s, H_{Py}). Found, %: C 60.72; H 5.09; N 8.83. C₁₆H₁₆N₂O₃S. Calculated, %: C 60.74; H 5.10; N 8.85.

Thienopyridines 2b-c were obtained analogously. The end of the reaction in each specific case was monitored by thin-layer chromatography with 1:2 acetone-hexane as the eluent.

Methyl 4,6-Dimethyl-3-(pyrrolyl)thieno[2,3-*b*]pyridine-2-carboxylate (2b) was obtained in 88% yield; mp 139-140°C (ethanol). ¹H NMR spectrum (DMSO-*d*₆, 200 MHz), δ, ppm: 1.83 (3H, s, 4-CH₃); 2.57 (3H, s, 6-CH₃); 3.73 (3H, s, CO₂CH₃); 6.23 (2H, s, H_β); 6.72 (2H, s, H_α); 7.05 (1H, s, H_{Py}). Found, %: C 62.90; H 4.91; N 9.76. C₁₅H₁₄N₂O₂S. Calculated, %: C 62.92; H 4.93; N 9.84.

Kuban State Technological University, Krasnodar 350072, Russia; e-mail: organics@kubstu.ru. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 3, pp. 444-445, March, 2003. Original article submitted October 9, 2002.

Phenyl 4,6-Dimethyl-3-(1-pyrrolyl)thieno[2,3-*b*]pyridine-2-carboxylate (2c) was obtained in 93% yield; mp 130-131°C (DMF). ¹H NMR spectrum (DMSO-*d*₆, 200 MHz), δ, ppm: 1.93 (3H, s, 4-CH₃); 2.63 (3H, s, 6-CH₃); 6.27 (2H, s, H_β); 6.83 (2H, s, H_α); 7.07 (1H, s, H_{Py}); 7.09-7.37 (5H, m, C₆H₅). Found, %: C 68.93; H 4.62; N 8.01. C₂₀H₁₆N₂O₂S. Calculated, %: C 68.95; H 4.63; N 8.04.

N,N-Diphenyl-4-methoxymethyl-6-methyl-3-(1-pyrrolyl)thieno[2,3-*b*]pyridine-2-carboxamide (2d) was obtained in 88% yield; mp 148-149°C (ethanol). ¹H NMR spectrum (DMSO-*d*₆, 200 MHz), δ, ppm: 2.57 (3H, s, CH₃); 3.15 (3H, s, OCH₃); 3.83 (2H, s, OCH₂); 6.27 (2H, s, H_β); 6.53 (2H, s, H_α); 7.05-7.28 (11H, m, C₆H₅, H_{Py}). Found, %: C 71.48; H 5.10; N 9.24. C₂₇H₂₃N₃O₂S. Calculated, %: C 71.50; H 5.11; N 9.26.

4-Methoxymethyl-6-methyl-2-(4-nitrophenyl)-3-(1-pyrrolyl)thieno[2,3-*b*]pyridine (2e) was obtained in 86% yield; mp 201-202°C (DMF). ¹H NMR spectrum (DMSO-*d*₆, 200 MHz), δ, ppm (*J*, Hz): 2.65 (3H, s, CH₃); 3.23 (3H, s, OCH₃); 4.01 (2H, s, OCH₂); 6.32 (2H, s, H_β); 6.73 (2H, s, H_α); 7.27 (2H, d, *J* = 8.9, 2-H, 6-H); 7.37 (1H, s, H_{Py}); 8.12 (2H, d, *J* = 8.9, 3-H, 5-H). Found, %: C 63.29; H 4.51; N 11.05. C₂₀H₁₇N₃O₃S. Calculated, %: C 63.31; H 4.52; N 11.07.

REFERENCES

1. E. A. Kaigorodova, L. D. Konyushkin, M. E. Niyazymbetov, S. N. Kvak, V. N. Zaplishnyi, and V. P. Litvinov, *Izv. Akad. Nauk, Ser. Khim.*, 2215 (1994).
2. E. A. Kaigorodova, L. D. Konyushkin, E. Yu. Kambulov, and G. D. Krapivin, *Khim. Geterotsikl. Soedin.*, 1024 (1997).
3. E. A. Kaigorodova, V. K. Vasilin, L. D. Konyushkin, E. B. Usova, and G. D. Krapivin, *Molecules*, **5**, 1085 (2000).