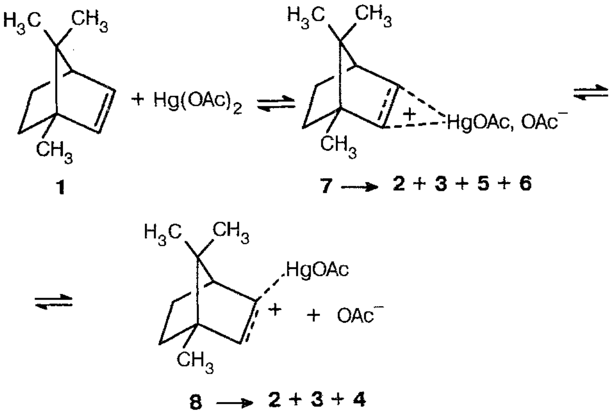
The data obtained imply that the reaction proceeds *via* at least two intermediates (**7**, **8**). In the absence of salts, the products are predominantly formed from solvated ion **8**. In the presence of the salt, the products are probably formed from ion **8** and ion pair **7** due to the effect of the common ion.



If the maximum concentrations of the salt are used (~0.015 *M*), then the **7** ⇌ **8** equilibrium is shifted toward ion pair **7**, and the reaction rate constant no longer depends on the additive concentration. In this case, the reaction products are formed from ion pair **7**. The regiochemical data and the composition of the reaction products indicate that ion pair **7** has a more symmetric structure than ion **8**.

The reaction rate was determined from changes in the concentration of $Hg(OCOCH_3)_2$ measured by the known procedure.[2] The composition of the reaction products after their demercuration with $NaBH_4$ or sodium amalgam was analyzed by GLC.

References

1. I. C. Ambidge, S. K. Dwight, C. M. Rynard, and T. T. Tidwell, *Can. J. Chem.*, 1977, **55**, 3086.
2. S. Fukuzumi and J. K. Kochi, *J. Am. Chem. Soc.*, 1981, **103**, 2783.

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Interaction of 3-amino-2-carbamoyl-5,6-trimethylene- and 3-amino-2-carbamoyl-5,6-hexamethylenethieno[2,3-*b*]pyridines with acetic anhydride

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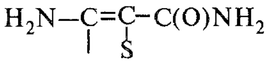
3-Amino-2-carbamoylthieno[2,3-*b*]pyridines substituted at the pyridine ring are used for synthesizing 4-oxopyrido[2′,3′:5,4]thieno[2,3-*d*]pyrimidines.[1]

We have found that the direction of the reaction of 5,6-polymethylene-3-amino-2-carbamoylthieno[2,3-*b*]-pyridines with acetic anhydride depends on the size of the polymethylene cycle. Refluxing 3-amino-2-carbamoyl-5,6-hexamethylenethieno[2,3-*b*]pyridine (**1a**) with acetic anhydride results in 2-methyl-4-oxopyrido-[2′,3′:5,4]thieno[2,3-*d*]pyrimidine (**2**), which exists in two tautomeric forms (**2a** and **2b**) in the ratio 2:1 (Scheme 1).

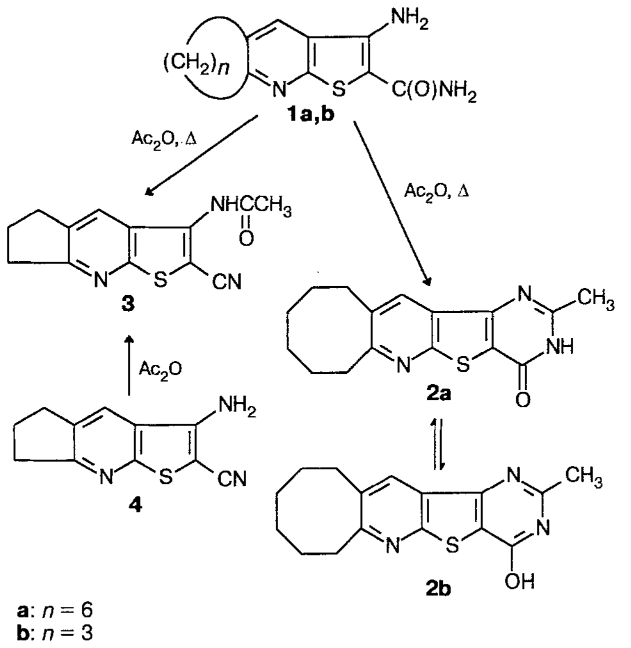
The reaction starting from 3-amino-2-carbamoyl-5,6-trimethylenethienopyridine (**1b**) proceeds in another direction and unexpectedly affords 3-acetylamino-2-cyanothieno[2,3-*b*]pyridine (**3**). The latter was also obtained by an independent synthesis from 3-amino-2-cyano-5,6-trimethylenethieno[2,3-*b*]pyridine (**4**). Obviously, the reaction follows this path due to increased strain in the thienopyridine unit, violation of the coplanar state of the aromatic thieno[2,3-*b*]pyridine bicycle, and a change in the electronic conjugation in the


$H_2N\text{—}\underset{|}{C}\text{=}\underset{S}{C}\text{—}C(O)NH_2$ fragment.

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 1, pp. 181—182, January, 1994.

1066-5285/94/4301-0177 $12.50

Scheme 1



IR spectra of the compounds were recorded on UR-20 and Perkin Elmer-457 spectrophotometers in KBr pellets. ^{1}H NMR spectra were obtained on a Bruker WM-250 spectrometer (250 MHz, DMSO-d_6, TMS as the internal standard). The purity of the compounds obtained was monitored by TLC on Silufol-254 plates in the acetone—heptane system (3:5). The chromatograms were visualized by iodine vapors.

A mixture of substituted pyridine **1a** (0.28 g, 0.001 mol) and acetic anhydride (10 mL) was refluxed for 1 h and cooled, then water (5 mL) was added. The residue was filtered off and washed with water, ethanol, and hexane to give 0.08 g (28 %) of compound **2**, m.p. > 300 °C. Found (%): C, 64.9; H, 5.2; N, 13.8; S, 10.7. $C_{16}H_{17}N_3OS$. Calculated (%): C, 64.5; H, 5.7; N, 14.0; S, 10.5. IR (KBr), ν/cm^{-1}: 1670 (δNH); 1720 (CO); 3268 (NH). ^{1}H NMR (DMSO-d_6), δ: 1.33 (m, 4 H, C(7)H$_2$, C(8)H$_2$); 1.74 (m, 4 H, C(6)H$_2$, C(9)H$_2$); 2.50 (s, 3 H, CH$_3$ in tautomer **b**); 2.54 (s, 3 H, CH$_3$ in tautomer **a**); 2.96 (m, 2 H, C(5)H$_2$); 3.07 (m, 2 H, C(10)H$_2$); 8.05 (s, H, C(4)H in tautomer **a**); 8.28 (s, H, C(4)H in tautomer **b**); 10.62 (s, H, OH); 12.76 (s, H, NH).

Similarly, product **3** was obtained from compounds **1b** or **4** in 57 or 78 % yield, respectively, m.p. 272—274 °C. Found (%): C, 60.9; H, 4.5; N, 15.9; S, 12.7. $C_{13}H_{11}N_3OS$. Calculated (%): C, 60.7; H, 4.2; N, 16.3; S, 12.4. IR (KBr), ν/cm^{-1}: 1678 (δCONH); 2216 (CN); 3236 (CONH); 3432 (br, NH). ^{1}H NMR (DMSO-d_6), δ: 2.15 (m, 2 H, C(6)H$_2$); 2.21 (s, 3 H, CH$_3$); 3.03 (q, 4 H, C(5)H$_2$, C(7)H$_2$); 8.13 (s, H, C(4)H); 10.68 (s, H, NH).

References

1. V. P. Litvinov, L. A. Rodinovskaya, Yu. A. Sharanin, A. M. Shestopalov, and A. Senning, *Sulfur Reports*, 1992, **13**, 1.

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Unusual insertion of product the reaction of 3,3-dichloropentanedione with aromatic aldehydes

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In the reaction of 3,3-dichloropentanedione with aromatic aldehydes under the conditions of alkali catalysis 4-acetoxy-4-aryl-3,3-dichloro-2-butanones (**1**) which are the products of the insertion of aromatic aldehydes into 3,3-dichloropentanedione at C_2—C_3, are formed, and not the expected α-chloroepoxides (**2**)

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