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FORMATION OF BISPYRIDYL DERIVATIVES DURING THE KOST–SAGITULLIN REARRANGEMENT

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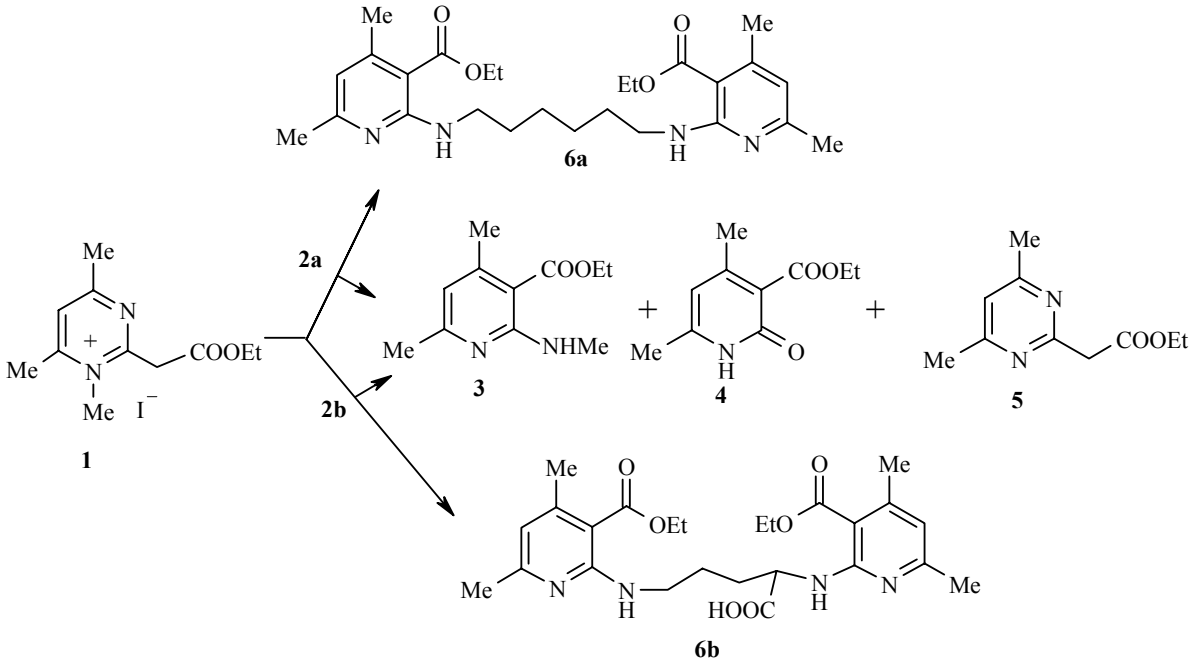
The Kost–Sagitullin rearrangement in the azinium salt series generally has been studied using treatment with amines [1, 2]. We know that reaction of pyrimidinium salts with such diamines as hydrazine and amidine derivatives leads to formation of pyrazole, triazole, or pyrimidine derivatives [3, 4].

We studied the reactions of 2-(ethoxycarbonyl)methyl-1,4,6-trimethylpyrimidinium iodide (**1**) with hexamethylenediamine **2a** and ornithine **2b**, which are compounds containing two primary amino groups. In both experiments, in addition to the rearrangements that are typical [5] of these reactions (pyridine **3** and pyridone **4**, and also pyrimidine **5**), compounds were isolated (**6a** and **6b** respectively) for which the ^{1}H and ^{13}C NMR spectra and the elemental analysis data suggested participation of both amine groups in a "rearrangement with transamination." The latter was observed for the first time not only in Kost–Sagitullin rearrangements but also for the better studied Dimroth rearrangement.



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The ^{1}H and ^{13}C NMR spectra were obtained on a Varian Mercury 300 spectrometer (300 MHz and 76 MHz respectively), internal standard TMS.

Reaction of Salt 1 with Hexamethylenediamine 2a. A mixture of salt **1** (1.35 g, 4 mmol) and amine **2a** (0.46 g, 4 mmol) was heated in absolute ethanol (12 ml) for 30 h. The crystals formed were filtered out and 0.19 g (20%) of N,N'-di(3-ethoxycarbonyl-4,6-dimethyl-2-pyridyl)hexamethylenediamine (**6a**) was obtained; mp 118-119°C, R_f 0.7 (Silufol, 6:1 toluene–acetone). Preparative separation of the filtrate on a column (4:1 toluene–acetone) was used to obtain 0.13 g (16%) of pyridine **3** (0.05 g, 6%), pyridone **4**, and pyrimidine **5** (0.1 g, 13%). The ^{1}H NMR spectrum of compound **6a** (DMSO-d_6), δ, ppm (*J*, Hz): 1.37 (6H, t, *J* = 7.1, $OCH_2\underline{CH_3}$); 1.47 (4H, m, γ- and γ'-CH_2); 1.64 (4H, m, β- and β'-CH_2); 2.29 (6H, s, 4- and 4'-CH_3); 2.38 (6H, s, 6- and 6'-CH_3); 3.46 (4H, br. m, α- and α'-CH_2); 4.29 (4H, q, *J* = 7.1, 3- and 3'-OCH_2); 6.17 (2H, s, H-5 and -5'); 7.89 (2NH, br. s, 2- and 2'-NH). Found, %: C 66.73; H 7.29; N 12.29. $C_{26}H_{34}N_4O_4$. Calculated, %: C 66.92; H 7.35; N 12.01.

Reaction of Salt 1 with Ornithine 2b. Ornithine hydrochloride **2b** (0.9 g, 5 mmol) and salt **1** (1.7 g, 5 mmol) were added to a solution of sodium ethoxide prepared from sodium (0.115 g, 5 mmol) and absolute ethanol (7 ml). The mixture was heated for 35 h. The solvent was distilled off and the residue was washed with chloroform. Obtained from a chloroform extract by preparative separation on a column (4:1 hexane–acetone): 0.3 g (25%) of 2,5-di[(3'-ethoxycarbonyl-4',6'-dimethyl-2'-pyridyl)amino]pentanoic acid (**6b**); mp 148-149°C, R_f 0.59 (3:1 toluene–acetone), pyridine **3** (0.1 g, 10%), pyridone **4** (0.2 g, 21%), and compound **5** (0.18 g, 18%).

Compound 6b. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 1.38 (3H, t, *J* = 7.1, OCH_2CH_3); 1.39 (3H, t, *J* = 7.1, OCH_2CH_3); 1.74-1.83 (2H, m, 4-CH_2); 1.96 (1H, m, 3-CH_2); 2.21 (1H, m, 3-CH_2); 2.30 (3H, s, 5-(4'-CH_3)); 2.39 (3H, s, 5-(6'-CH_3)); 2.40 (3H, s, 2-(4'-CH_3)); 2.50 (3H, s, 2-(6'-CH_3)); 3.55 (2H, br. m, $NHCH_2$); 4.32 (2H, q, *J* = 7.1, 5-OCH_2); 4.36 (2H, q, *J* = 7.1, 2-OCH_2); 4.38 (2H, br. m, NHCH); 6.21 (H, s, H-5 (-5')); 6.42 (H, s, H-2(-5')); 7.83 (NH, br. t, *J* = 5.3, $NHCH_2$); 8.13 (NH, br. d, *J* = 4.9, NHCH). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 14.32 (5-(4'-CH_3)); 14.42 (2-(4'-CH_3)); 23.71 (5-(6'-CH_3)); 23.89 (2-(6'-CH_3)); 26.18 (4-CH_2); 28.08 (3-CH_2); 40.62 ($NHCH_2$); 56.42 (CH); 60.58 (5-OCH_2); 61.39 (2-OCH_2); 103.94 (5-C(5')); 106.43 (2-C(5')); 114.96 (5-C(3')); 117.05 (2-C(3')); 151.27 (5-C(4')); 154.00 (2-C(4')); 158.42 (5-C(6')); 158.72 (2-C(6')); 159.11 (5-C(2')); 160.88 (2-C(2')); 168.08 (5-C=O); 169.19 (2-C=O); 173.33 (COOH). Found, %: C 61.63; H 7.39; N 11.59. $C_{25}H_{36}N_4O_6$. Calculated, %: C 61.46; H 7.43; N 11.47.

Compound: 3 (R_f 0.62 (4:1 toluene–acetone), **4** R_f 0.52 (1:2 toluene–acetone), and **5** R_f 0.67 (1:1 toluene–acetone).

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