Chemistry of Heterocyclic Compounds, Vol. 35, No. 10, 1999

TRANSAMINATION OCCURRING IN THE ENAMINE REARRANGEMENT OF PYRIMIDINIUM SALTS IN REACTION WITH BENZYLAMINE

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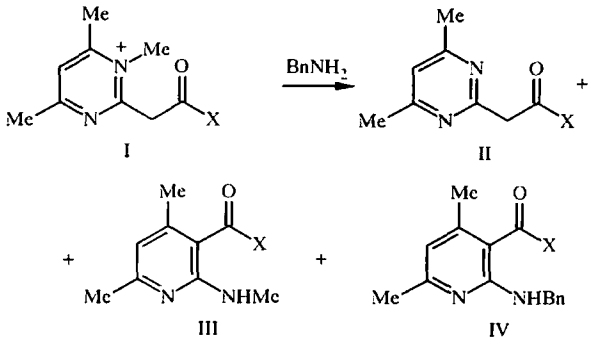
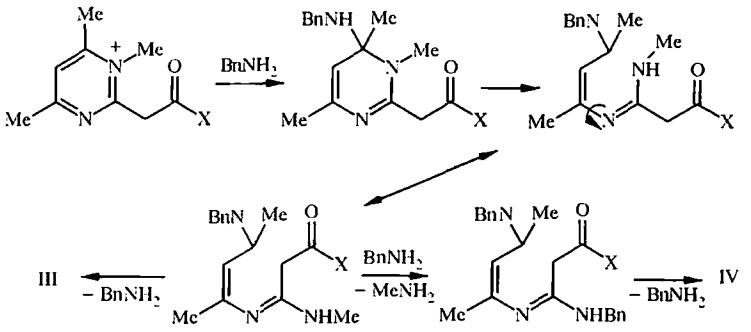
Treatment of 2-(carbethoxymethyl)-1,4,6-trimethylpyrimidinium iodide (Ia) and the corresponding amide Ib with benzylamine leads to demethylation and the expected enamine rearrangement [1, 2] (i.e. formation of the pyrimidines IIa,b and 2-methylaminopyridines IIIa,b) together with the formation of products due to exchange of the amine fragment of the enamine rearrangement, *viz.* the 2-benzylamino-4,6-dimethylnicotinic acid derivatives IVa,b.



a X = OEt, b X = NH_2

It is suggested that, at the stage of the open form V, exchange of the amine group occurs and this leads to formation of a transaminated, recyclized product.



Exchange of an amine fragment in the rearrangement of pyrimidines to pyridines has not been reported previously.

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Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 10, pp. 1434-1435, October, 1999. Original article submitted April 16, 1999.

0009-3122/99/3510-1251$22.00©1999 KluwerAcademic/Plenum Publishers

2-Benzylamino-4,6-dimethylnicotinic Acid Amide (IVb). A mixture of iodide Ib (0.5 g, 1.6 mmol) and benzylamine (5 ml) was heated in a sealed ampul for 15 h at 95-100°C. Excess amine was distilled off and the residue was treated with hot hexane and separated on a silica gel column (5/40) using benzene–acetone (1:1) to give IVb (180 mg, 45%), nicotinamide IIIb (70 mg, 24%), and pyrimidine IIb (40 mg, 15%).

An experiment with iodide Ia (0.7 g, 2 mmol) was carried out similarly to give pyrimidine IIa (50 mg, 15%), compound IIIa (120 mg, 30%), and ethyl 2-benzylamino-4,6-dimethylnicotinate (IVa, 200 mg, 35%).

Compound IVa. Oil. R_f 0.77 (benzene–acetone, 10:1). ^{1}H NMR spectrum ($CDCl_3$): 1.35 (3H, t, J = 7.2 Hz, $OCH_2\underline{CH_3}$); 2.34 (3H, s, 6(4)-CH_3); 2.44 (3H, s, 4(6)-CH_3); 4.33 (2H, q, J = 7.2 Hz, $O\underline{CH_2}CH_3$); 4.75 (2H, d, J = 5.5 Hz, $NH\underline{CH_2}$,Ph); 6.28 (1H, s, 5-H); 7.23-7.40 (5H, m, Ph); 8.1 ppm (1H, br. s, NH). Found, %: C 71.70; H 6.94; N 9.68. $C_{17}H_{20}N_2O_2$. Calculated, %: C 71.81; H 7.09; N 9.85.

Compound IVb. Mp 146-147°C. R_f 0.65 (benzene–acetone, 1:1). ^{1}H NMR spectrum ($CDCl_3$): 2.34 (3H, s, 6(4)-CH_3); 2.35 (3H, s, 4(6)-CH_3); 4.67 (2H, d, J = 5.4 Hz, $NHCH_2Ph$); 5.71 (2H, br s, NH_2); 6.29 (1H, s, 5-H); 6.35 (1H, br. s, $\underline{NH}CH_2Ph$); 7.21-7.37 ppm (5H, m, Ph). Found, %: C 70.71; H 6.65; N 16.59. $C_{15}H_{17}N_3O$. Calculated, %: C 70.56; H 6.71; N 16.46.

According to chromatographic and ^{1}H NMR spectral data, compounds II and III were identical to a known sample [1]. NMR Spectra were obtained on a Varian Mercury 300 spectrometer in the Center for Research of the Structure of Molecules, Armenian National Academy of Sciences (program US CRDF RESC 17-5).

This work was carried out within the scope of the science package 96-559 of the Ministry of science and education of the Armenian Republic, the joint grant ACH-006 98/AC1-955 of the National fund for science and advanced technology in Armenia (NFSAT), and the United States fund for civic research and development (US CRDF).

The authors thank Professor Alan Katritzky for support and for useful discussions.

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