

SHORT  
COMMUNICATIONS

## 2-Aminopyridine Condensation with Formaldehyde

B. F. Kukharev, V. K. Stankevich, G. R. Klimenko, and V. A. Kukhareva

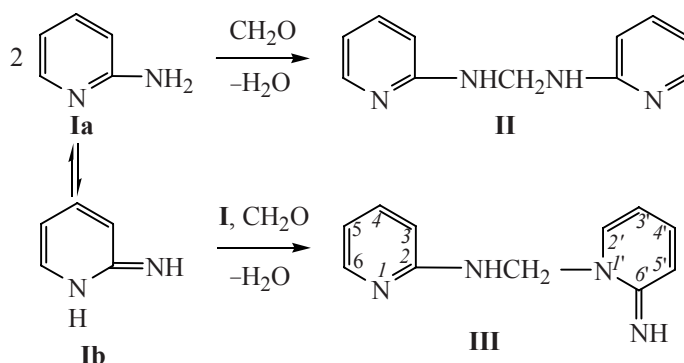
Faworsky Irkutsk Institute of Chemistry, Siberian Division, Russian Academy of Sciences,  
Irkutsk, 664033 Russia  
e-mail: irk\_inst\_chem@irioch.irk.ru

Received March 12, 2009

DOI: 10.1134/S1070428009080260

The condensation products of 2-aminopyridine (**I**) with aldehydes are regarded as *N,N'*-di(2-pyridyl)methylnediamine derivatives **II** [1]. It was in particular reported

that in the condensation of 2-amino-pyridine (**I**) with formaldehyde formed *N,N'*-di(2-pyridyl)methylnediamine (**II**) [2].



We found that in this reaction alongside the symmetric compound **II** the condensation of formaldehyde with 2-aminopyridine (**Ia**) and its tautomer 2-pyridoneimine (**Ib**) afforded *N*-[2-imino-1(2*H*)-pyridyl]methylpyridine-2-amine (**III**). The presence of two isomeric compounds is revealed by the appearance in the  $^1\text{H}$  NMR spectrum of a triplet and a doublet from the protons of methylene groups,  $\delta$  5.01 ( $\text{NHCH}_2\text{NH}$ ) and 5.25 ppm ( $\text{NHCH}_2\text{N}$ ) respectively. The spectrum contained also broadened triplets ( $\delta$  5.67 and 6.01 ppm) of amino groups from both isomers. In the  $^{13}\text{C}$  NMR spectrum the signals of carbon atoms of the methylene groups from isomers **II** and **III** have chemical shifts 49.25 and 56.17 ppm respectively. Besides the signals of the other protons and carbon atoms of both isomers are sufficiently well resolved in the spectra although sometimes the weaker

signals of isomer **III** are overlapped by the signals of isomer **II** preventing the establishment of the multiplicity and the coupling constants.

The reaction with the water solution of formaldehyde by procedure [2] or at boiling amine **I** with paraformaldehyde in benzene or xylene with the azeotrope distilling off the water led to the formation of practically the same mixture containing by  $^1\text{H}$  NMR data in all events from 7 to 9% of unsymmetrical isomer **III**.

A mixture of 47 g (0.5 mol) of 2-aminopyridine (**I**), 7.9 g (0.25 mol) of 95% paraformaldehyde, and 70 ml of benzene was boiled at reflux with a Dean-Stark trap till the end of water separation. On cooling to room temperature the precipitated crystals were filtered off, dried, and recrystallized from acetone. We obtained 43 g of mixture

containing according to  $^1\text{H}$  NMR data 91% of *N,N'*-di-(2-pyridyl)methylenediamine (**II**) and 9% of isomer **III**. Yield 86%, mp 125–127°C {mp 121–122°C (acetone) [2]}. IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 3390, 3380, 3230, 3180, 3150, 3115, 3080, 3050, 3015, 2980, 2965, 2925, 1595, 1570, 1505, 1490, 1445, 1410, 1385, 1330, 1300, 1275, 1225, 1155, 1140, 1105, 980, 850, 830, 800, 770, 730, 645, 600, 495.  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm, isomer **II**: 5.01 t (2H,  $\text{CH}_2$ ,  $^3J$  6.4 Hz), 5.67 br.t (2H,  $\text{NHCH}_2\text{NH}$ ), 6.36 d (2H,  $2\text{C}^3\text{H}$ ,  $^3J_{3,4}$  8.3 Hz), 6.54 m (2H,  $2\text{C}^5\text{H}$ ), 7.32 m (2H,  $2\text{C}^4\text{H}$ ), 8.07 d (2H,  $2\text{C}^6\text{H}$ ,  $^3J_{5,6}$  4.9 Hz); isomer **III**: 5.25 d (2H,  $\text{CH}_2$ ,  $^3J$  6.4 Hz), 5.6 br.s (1H, =NH), 6.01 br.t (1H,  $\text{NHCH}_2$ ), 6.30 d (1H,  $\text{C}^6\text{H}$ ,  $^3J_{6,5}$  8.3 Hz), 6.42–6.6 m (4H,  $\text{C}^3\text{H}$ ,  $\text{C}^4\text{H}$ ,  $\text{C}^5\text{H}$ ,  $\text{C}^5\text{H}$ ), 6.97 d (1H,  $\text{C}^3\text{H}$ ,  $^3J_{3,4}$  8.5 Hz), 7.40 m (1H,  $\text{C}^4\text{H}$ ), 8.12 d (1H,  $\text{C}^6\text{H}$ ,

$^3J_{5,6}$  4.6 Hz).  $^{13}\text{C}$  NMR spectrum,  $\delta$ , ppm, isomer **II**: 49.25 ( $\text{CH}_2$ ), 109.53 ( $\text{C}^3$ ), 113.49 ( $\text{C}^5$ ), 137.16 ( $\text{C}^4$ ), 148.00 ( $\text{C}^6$ ), 158.09 ( $\text{C}^2$ ); isomer **III**: 56.17 ( $\text{CH}_2$ ), 108.54 ( $\text{C}^3$ ), 109.47 ( $\text{C}^3$ ), 113.27 ( $\text{C}^5$ ), 114.84 ( $\text{C}^5$ ), 137.24 ( $\text{C}^4$ ), 137.48 ( $\text{C}^4$ ), 147.65 ( $\text{C}^6$ ), 147.84 ( $\text{C}^6$ ), 157.84 ( $\text{C}^2$ ), 158.13 ( $\text{C}^2$ ). Found, %: C 66.11; H 6.06; N 27.87.  $\text{C}_{11}\text{H}_{12}\text{N}_4$ . Calculated, %: C 65.98; H 6.04; N 27.98.

#### REFERENCES

1. Smit, D.M., in *Comprehensive Organic Chemistry*, Barton, D. and Ollis, W.D., Eds., Oxford: Pergamon, 1979, vol. 8.
2. Marzona, M. and Carpignano, R., *Ann. Chem. (Rome)*, 1965, vol. 55, p. 1007; *Chem. Abstr.*, 1966, vol. 64, 6607b.