ISSN 1070-3632, Russian Journal of General Chemistry, 2007, Vol. 77, No. 2, pp. 307–308. © Pleiades Publishing, Ltd., 2007.
Original Russian Text © O.S. Attaryan, G.A. Akopyan, K.S. Badalyan, G.V. Asratyan, 2007, published in Zhurnal Obshchei Khimii, 2007, Vol. 77, No. 2, pp. 335–336.

LETTERS TO THE EDITOR

Bromination of 1,3-Dimethyl- and 1,5-Dimethyl-1*H*-pyrazole-4-carboxylic Acids

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Received November 22, 2006

DOI: 10.1134/S1070363207020193

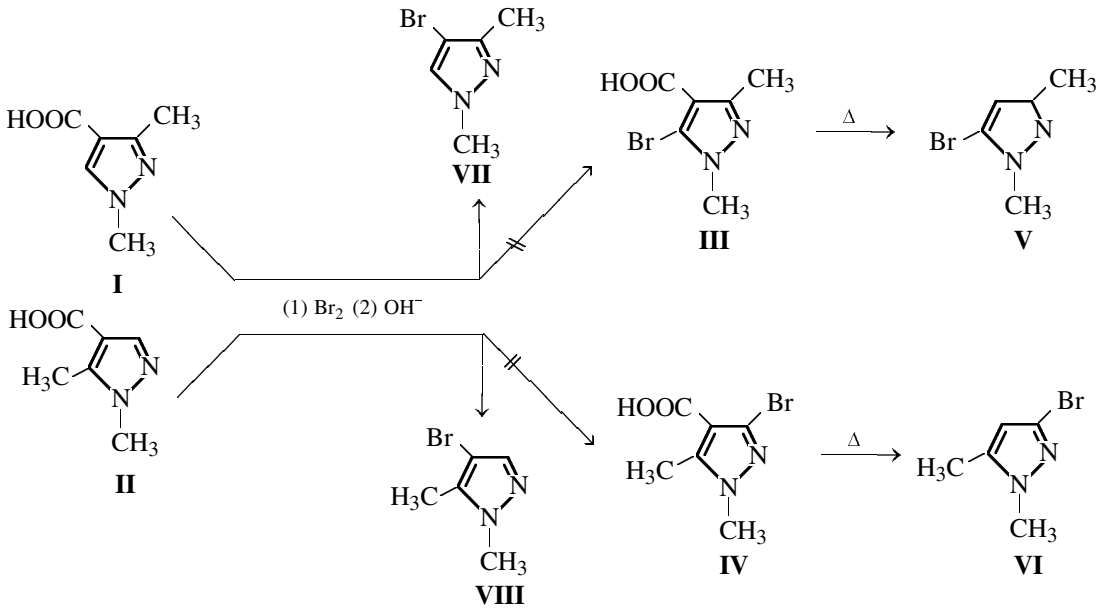
Bromination is a common method for preparing pyrazole bromo derivatives; therewith, no catalysts are required. In anhydrous organic solvents, the product forms as hydrobromide. However, if the process is carried out with the conjugate base of pyrazole, 4-bromopyrazole is isolated directly [1]. With excess bromine, dibromo and tribromo derivatives can form [2].

According to [3, 4], *N*-methyl(ethyl)pyrazole-3(5)-carboxylic acids are brominated exclusively at the 4 position of the pyrazole ring.

We expected that bromination of 1,3-dimethyl- and 1,5-dimethyl-1*H*-pyrazole-4-carboxylic acids (**I**, **II**) followed by decarboxylation of products **III**, **IV** would allow us to prepare 5-bromo-1,3-and 3-bromo-1,5-dimethyl-1*H*-pyrazoles (**V**, **VI**).

However, upon bromination of acids **I**, **II** we isolated from the reaction mixtures 4-bromo derivatives **VII**, **VIII** (yield 70–80%), instead of desired products **III**, **IV**.

The structure of compounds **VII**, **VIII** was proved by their independent synthesis via bromination of 1,3-dimethyl- and 1,5-dimethylpyrazoles, as well as by ^{1}H NMR and IR spectroscopy, GLC, and elemental analysis.



The IR spectra were recorded on a Specord 75 UR spectrophotometer in KBr pellets or in thin films. The ^{1}H NMR spectra were measured on a Varian–Mercury instrument (300 MHz) in DMSO-d_6 solutions.

Starting pyrazoles **I** and **III** were prepared as described in [6, 7]: **I**, mp 182°C; **II**, mp 186°C.

4-Bromo-1,3-dimethyl-1*H*-pyrazole (VII). To a solution of 14 g of 1,3-dimethyl-1*H*-pyrazole-4-carboxylic acid in 100 ml of water, 4 g of sodium hydroxide was added, and then 16 g of bromine was added dropwise at room temperature over the course of 1 h. The reaction mixture was neutralized with 2 N HCl, extracted with chloroform (3 × 50 ml), and dried over $MgSO_4$. The solvent was removed, and the residue was distilled in a vacuum to obtain 14 g (80%) of compound **VII**, bp 45°C (1 mm Hg), n_D^{20} 1.521, d_4^{20} 1.5059 [5]. IR spectrum, ν, cm^{-1}: 1510 (pyrazole ring). ^{1}H NMR spectrum, δ, ppm: 2.15 s (3H, 3-CH_3), 3.81 s (3H, N–CH_3), 7.51 s (1H, 5-H). Found, %: C 34.38; H 4.31; Br 45.88; N 16.43. $C_5H_7BrN_2$. Calculated, %: C 34.31; H 4.02; Br 45.65; N 16.00.

4-Bromo-1,5-dimethyl-1*H*-pyrazole (VIII) was prepared similarly to **VII** from 14 g of 1,5-dimethyl-1*H*-pyrazole-4-carboxylic acid and 16 g of bromine, yield 12.3 g (70%), bp 52°C (1 mm Hg), n_D^{20} 1.521, d_4^{20} 1.5059 [5]. IR spectrum, ν, cm^{-1}: 1530 (pyrazole ring). ^{1}H NMR spectrum, δ, ppm: 2.25 s (3H, 3-CH_3), 3.80 s (3H, N–CH_3), 7.21 s (1H, 5-H). Found, %: C 34.49; H 4.42; Br 45.93; N 16.51. $C_5H_7BrN_2$. Calculated, %: C 34.31; H 4.02; Br 45.65; N 16.00.

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