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LETTERS TO THE EDITOR

Bromination of 1,3-Dimethyl- and 1,5-Dimethyl-4-hydroxymethylpyrazoles

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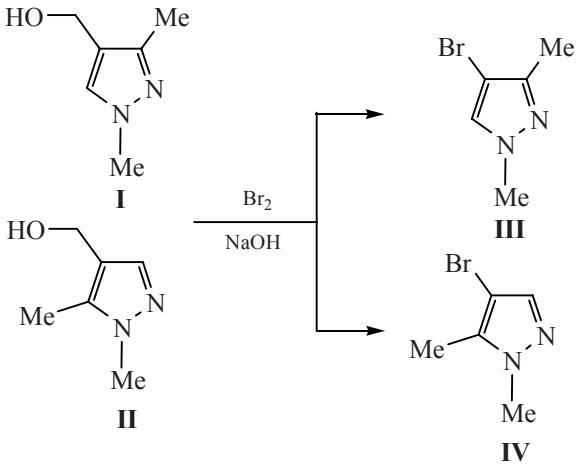
Ambiguous behavior in the bromination of 4-formylpyrazoles [1, 2] and 4-pyrazolecarboxylic acids [3] was mentioned earlier. In the presence of sodium hydroxide the reaction proceeds as substitution of carbonyl (carboxy) group with the bromine atom.

4-Hydroxymethylpyrazole hydroxy group seems to be a convenient functional substituent for purposeful synthetic transformations [4].

In continuation of the search for synthetic pathways to 1,3-dimethyl-5-bromo- and 1,5-dimethyl-3-bromopyrazoles we studied in this work the bromination of 1,3-dimethyl- and 1,5-dimethyl-4-hydroxymethylpyrazoles **I** and **II** [1–3, 5]. The results of the investigation show that bromination of 4-hydroxymethylpyrazoles in the water–alkali medium leads to substitution of hydroxymethyl group with the bromine atom:



The structure of compounds **III** and **IV** was established on the basis of ^{1}H NMR and IR spectroscopy and elemental analysis data.

In the ^{1}H NMR spectra signals of methyl and hydroxy group protons at δ 4.20 and 3.97 ppm are absent. Integral intensities of the others protons correspond fully to the structures of 1,3-dimethyl- and 1,5-dimethyl-4-bromopyrazoles **III** and **IV**.

1,3-Dimethyl-4-bromopyrazole (III). To a mixture of 13.0 g of 1,3-dimethyl-4-hydroxymethylpyrazole **I**, 100 ml of water, and 12 g of sodium hydroxide was added dropwise 16 g of bromine at room temperature within 1 h. Then the product was extracted with chloroform (3×50 ml) and dried over $MgSO_4$. When the solvent was removed, the residue was distilled in vacuum. Yield 12.6 g (72%), bp 47°C (1 mm Hg), n_D^{20} 1.5210 [1, 6]. IR spectrum, ν, cm^{-1}: 1510 (ring). ^{1}H NMR spectrum, δ, ppm: 2.14 s (3H, 3-CH_3), 3.80 s (3H, N–CH_3), 7.50 s (1H, 5-H). Found, %: C 34.26; H 4.35; Br 45.80; N 16.43. $C_5H_7BrN_2$. Calculated, %: C 34.29; H 4.00; Br 45.71; N 16.00.

1.5-Dimethyl-4-bromopyrazole (IV) was prepared similarly from 13.0 g of 1,5-dimethyl-4-hydroxymethylpyrazole **II**. Yield 11.4 (65%), bp 53°C (1 mm Hg), mp 43°C [1, 6]. IR spectrum, ν, cm^{-1}: 1530 (ring). ^{1}H NMR spectrum, δ, ppm: 2.25 s (3H, 5-CH_3), 3.80 s (3H, N–CH_3), 7.21 s (1H, 3-H). Found, %: C 34.71; H 4.48; Br 45.82; N 16.57. $C_5H_7BrN_2$. Calculated, %: C 34.29; H 4.00; Br 45.71; N 16.00.

The IR spectra were taken on a Specord-75 IR spectrophotometer (KBr pellets, film). The ^{1}H NMR

spectra were registered on a Varian Mercury-300 instrument (300 MHz) in DMSO-d_6. The starting pyrazoles **I** (mp –60°C) and **II** (mp –82°C) were prepared by the known procedure [7, 8].

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