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LETTERS TO THE EDITOR

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

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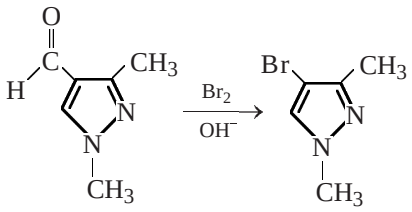
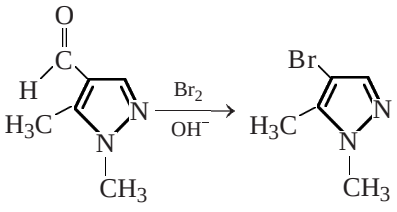
Proceeding with the search for synthetic approaches to 5-bromo-1,3-dimethyl- and 3-bromo-1,5-dimethylpyrazoles [1] we have studied bromination of 1,3-dimethyl- and 1,5-dimethyl-1*H*-pyrazole-4-carbaldehydes (**I, II**). It was found that the reaction in aqueous alkali involves substitution of the formyl group by bromine by the following scheme:



I **III**



II **IV**

The structure of compounds **III** and **IV** was established by means of IR and ^{1}H NMR spectroscopy and elemental analysis. The ^{1}H NMR spectrum contains no aldehyde proton signal at δ 9.78 ppm, and the IR spectrum shows no bands at 1680 cm^{-1} related to the formyl group. The integral intensities of the rest protons are completely consistent with the suggested structures.

Starting pyrazoles **I** and **I** were prepared by known procedures [2, 3], mp 50 and 60°C, respectively.

4-Bromo-1,3-dimethyl-1*H*-pyrazole (III) To a solution of 12.5 g of 1,3-dimethyl-1*H*-pyrazole-4-carbaldehyde (**I**) in 100 ml of water, 12 g of NaOH was added and then 16 g of bromine was added dropwise at room temperature. The reaction mixture was then extracted with chloroform (3 × 50 ml), the extract was dried over $MgSO_4$, the solvent was removed, and the residue was distilled in a vacuum to obtain 12 g (69%) of compound **III**, bp 45°C (1 mm Hg), n_D^{20} 1.521, d_4^{20} 1.4059 [1, 4]. 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, H^4). 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 (IV) was obtained in a similar way from 12.4 g of 1,5-dimethyl-1*H*-pyrazole-4-carbaldehyde (**II**) and 16 g of bromine. Yield 11 g (63%), bp 54°C (1 mm Hg), mp 43°C [1, 4]. 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, H^4). Found, %: C 34.62, H 4.42, Br 45.89, N 16.58. $C_5H_7BrN_2$. Calculated, %: C 34.31, H 4.02, Br 45.65, N 16.00.

The ^{1}H NMR spectra were taken on a Varian Mercury-300 spectrometer in DMSO-d_6. The IR spectra were obtained on a Specord IR-75 spectrometer in KBr pellets and in thin layer.

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