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SHORT COMMUNICATIONS

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

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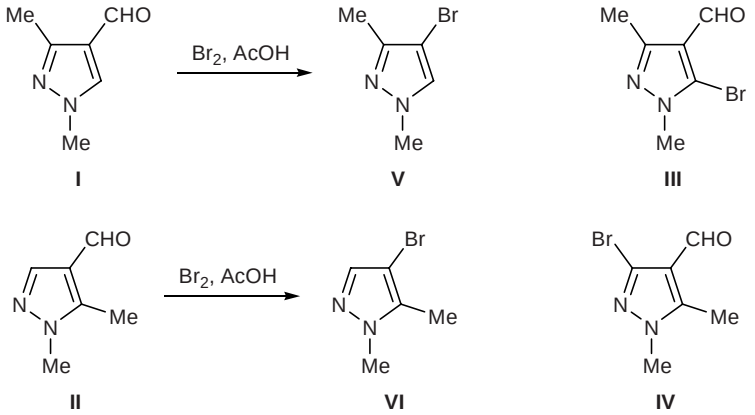
With a view to obtain 5-bromo-1,3-dimethyl-1*H*-pyrazole and 3-bromo-1,5-dimethyl-1*H*-pyrazole we tried to perform bromination of 1,3-dimethyl-1*H*-pyrazole-4-carbaldehyde (**I**) and 1,5-dimethyl-1*H*-pyrazole-4-carbaldehyde (**II**) with subsequent oxidation and decarboxylation. Surprisingly, instead of the expected products **III** and **IV**, the bromination of formylpyrazoles **I** and **II** gave 4-bromo-1,3-dimethyl-1*H*-pyrazole (**V**) and 4-bromo-1,5-dimethyl-1*H*-pyrazole (**VI**). The structure of products **V** and **VI** was proved by independent synthesis, bromination of 1,3-dimethyl- and 1,5-dimethyl-1*H*-pyrazoles [1], as well as by the data of ^{1}H NMR and IR spectroscopy and elemental analysis.

Initial pyrazolecarbaldehydes **I** and **II** were synthesized by the procedures described in [2]; **I**, mp 50°C; **II**; mp 60°C.

4-Bromo-1,3-dimethyl-1*H*-pyrazole (V). 1,3-Dimethyl-1*H*-pyrazole-4-carbaldehyde (**I**), 12.4 g (0.1 mol), was dissolved in 50 ml of acetic acid, 16 g (0.1 mol) of bromine was added at 20–25°C, and the mixture was heated to 100°C and kept for 10 h at that temperature. After cooling, the mixture was neutralized with 2 N NaOH and treated with chloroform (100 ml), the extract was dried over $MgSO_4$, the solvent was removed, and the residue was distilled under reduced pressure. Yield 15.7 g (90%), bp 45°C (1 mm), n_D^{20} = 1.5210, d_4^{20} = 1.5059 [3]. IR spectrum: ν 1510 cm^{-1} (pyrazole ring). ^{1}H NMR spectrum, δ, ppm: 2.15 s (3H, 3-CH_3), 3.81 s (3H, 1-CH_3), 7.51 s (1H, 5-H). Found, %: C 34.48; H 4.51; Br 45.88; N 16.23. $C_5H_7BrN_2$. Calculated, %: C 34.31; H 4.02; Br 45.65; N 16.00.

4-Bromo-1,5-dimethyl-1*H*-pyrazole (VI) was synthesized in a similar way from 12.4 g (0.1 mol) of 1,5-dimethyl-1*H*-pyrazole-4-carbaldehyde (**II**) and 16 g (0.1 mol) of bromine. Yield 14.8 g (85%), bp 52°C (1 mm), mp 43°C; published data [4]: bp 85°C



(10 mm), mp 38°C. IR spectrum: ν 1530 cm^{-1} (pyrazole ring). ^1H NMR spectrum, δ, ppm: 2.25 s (3H, 5-CH_3), 3.80 s (3H, 1-CH_3), 7.21 s (1H, 3-H). 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 IR spectra were recorded from samples prepared as KBr pellets on a Specord 75IR spectrometer. The ^1H NMR spectra were meas-ured on a Varian Mercury instrument operating at 300 MHz from solutions in DMSO-d_6.

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