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LETTERS TO THE EDITOR

Bromination of Pyrazole-3(5)-carboxylic Acid

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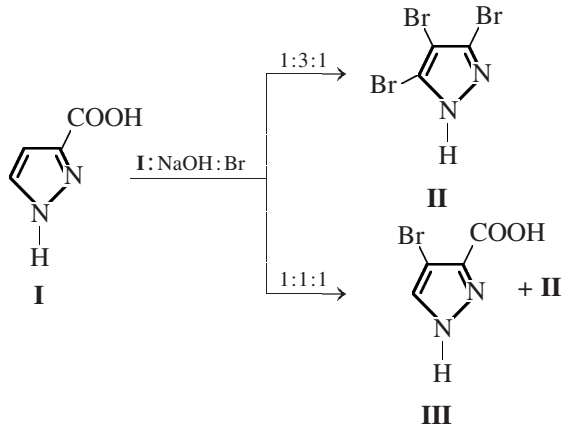
Earlier we showed [1] that the bromination of 1,3-dimethyl- and 1,5-dimethylpyrazole-4-carboxylic acids in the presence of sodium hydroxide involves substitution of the carboxy group by bromine.

These data gave us grounds to suggest that by brominating pyraxole-3(5)-carboxylic acid (**I**) under analogous conditions we could prepare hardly accessible 3(5)-bromopyrazole.



However, bromination of acid **I**, gave, instead of the expected product, 3,4,5-tribromopyrazole (**II**), yield 90%, mp 184°C [2].

With a 1 : 1 : 1 molar ratio of **I**, NaOH, and Br_2, the yield of compound **II** sharply falls (8.8%), and the major reaction product (90%) in this case is 4-bromopyrazole-3(5)-carboxylic acid (**III**). 4-Bromopyrazole, mp 92°C, prepared by decarboxylation of compound **II**, is identical to the product prepared by direct bromination of pyrazole [2].

The structure of compounds **II**, **III** was proved by ^{1}H NMR spectroscopy, mass spectrometry, and elemental analysis. The positions and integral intensities of the NH and COOH signals in the ^{1}H NMR spectra of compounds **II**, **III** are fully consistent with the proposed structures. The ^{1}H NMR spectra were obtained on a Varian Mercury 300 instrument in $(CD_3)_2SO$. The mass spectrum was taken on an MX-1321A instrument (direct inlet, ionizing energy 60 eV).

3,4,5-Tribromopyrazole (II). Bromine, 16 g, was added dropwise at room temperature over the course of 1 h to a solution of 11.2 g of pyrazole-3(5)-carboxylic acid in 100 ml of water and 12 g of NaOH. Crystals formed and were filtered off and recrystallized to obtain 9 g (90% by volume) of compound **II**, mp 184°C (water + ethanol, 1 : 1). ^{1}H NMR spectrum (DMSO-d_6, 300 MHz), δ, ppm: 13–14 br (1H, NH). Mass spectrum, M^+: found: 305; calculated: 305. Found, %: C 12.25; H 0.52; N 9.53; Br 79.21. $C_3HN_2Br_3$. Calculated, %: C 11.80; H 0.33; N 9.18; Br 78.69.

4-Bromopyrazole-3(5)-carboxylic acid (III). Bromine, 16 g, was added dropwise at room temperature over the course of 1 h to a solution of 11.2 g of pyrazole-3(5)-carboxylic acid in 100 ml of water and 4 g of NaOH. The reaction mixture was stirred for 3 h at the same temperature. Crystals formed and were filtered off and dissolved in ethanol, after which ethanolic KOH (1 : 1) was added. The precipitate was filtered off and dissolved in water. The solution was acidified to obtain 17.2 g (90%) of compound **III**, mp 260°C (decomp.). ^{1}H NMR spectrum (DMSO-d_6, 300 MHz), δ, ppm: 7.91 s (1H, 5-H), 13–14 br (2H,

NH, COOH). Mass spectrum, M^+: found: 191; calculated: 191. Found, %: C 26.71; H 1.84; N 15.23; Br 42.15. $C_4H_3N_2O_2Br$. Calculated, %: C 25.13; H 1.57; N 14.66; Br 41.88. Hot water was added to the filtrate, and the precipitate that formed was filtered off to obtain 0.9 g (8.8%) of compound **II**, mp 184°C (water + ethanol, 1 : 1).

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