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LETTERS TO THE EDITOR

# Formation Pathway of Bis-(1,3,5-trimethylpyrazol-4-yl)methane at Chlorination of 4-Hydroxymethyl-1,3,5-trimethylpyrazole

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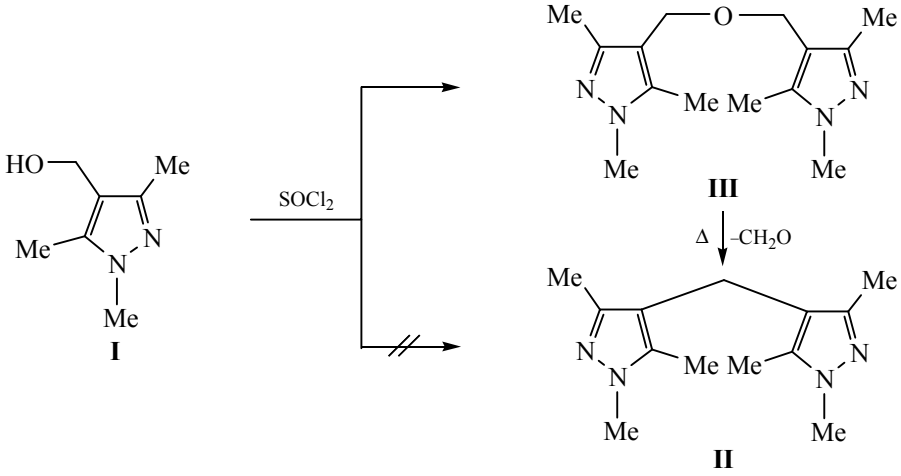
Synthesis of 4-chloromethylpyrazoles by 4-hydroxymethylpyrazoles chlorination was reported earlier [1]. Gandberg et al. failed to obtain 4-chloromethyl derivatives at the action of thionyl chloride on hydroxymethyl derivatives of 1-alkylpyrazoles. Compound **II** was found to be the reaction product. They believed that in 1-alkylpyrazoles series hydroxymethyl moiety in the position 4 is extremely labile and behaves as 1-oxymethyl group, which readily departed at the action of acidic agents [2]. Due to this compound **I** transforms smoothly into bis(1,3,5-trimethylpyrazol-4-yl)methane **II**.




We established that the chlorination of compound **I** results in the cross-coupling of two molecules of pyrazolecarbinols yielding the corresponding symmetric ether **III** [3]. The latter was found to undergo formaldehyde ejection at distillation to form compound **II** [4]. In the $^1$H NMR spectrum of compound **III** protons of the ether moiety appear as a singlet at δ 4.14 ppm; integral intensities fully correspond to the structure of compound **III**. The singlet signal of the methylene protons of compound **II** is shifted upfield in comparison with **III** (δ 3.31 ppm).

**Di-(1,3,5-trimethylpyrazol-4-yl)dimethyl ether (III).** To a mixture of 14 g of compound **I** and 50 ml of anhydrous carbon tetrachloride was slowly added dropwise 14 ml of thionyl chloride under stirring and cooling. The reaction mixture was stirred for 2 h at room temperature. Then to the mixture 25 ml of cold water was added under careful stirring. The aqueous layer was separated, neutralized with sodium carbonate, and extracted with butanol, after removal of the solvent the residue was distilled in a vacuum. Yield 8.2 g (67%), mp 68°C. IR spectrum, ν, cm$^{-1}$: 1590

(heterocycle), 1100 (COC). $^1$H NMR spectrum (DMSO-$d_6$), δ, ppm: 2.08 s (6H, 3-$CH_3$), 2.18 s (6H, 5-$CH_3$), 3.65 s (6H, N–$CH_3$), 4.14 s [4H, O$(CH_2)_2$]. Found, %: C 64.35; H 8.00; N 21.68. $C_{14}H_{22}N_4O$. Calculated, %: C 64.12; H 8.40; N 21.37.

**Bis(1,3,5-trimethylpyrazol-4-yl)methane (II)** was obtained by distillation of 0.1 mol of compound **III**. Yield 12.76 g (55%), mp 87°C (petroleum ether). IR spectrum, ν, cm$^{-1}$: 1550 (ring). $^1$H NMR spectrum (DMSO-$d_6$), δ, ppm: 1.98 s (6H, 3-$CH_3$), 2.00 s (6H, 5-$CH_3$), 3.31 s (2H, $CH_2$), 3.64 s (3H, N–$CH_3$). Found, %: C 67.55; H 8.32; N 24.45. $C_{13}H_{20}N_4$. Calculated, %: C 67.24; H 8.62; N 24.14.

The IR spectra were obtained on a Specord 75 IR instrument from KBr pellets in thin layer. The $^1$H NMR spectra were registered on a Varian-Mercury-300 instrument (300 MHz) in $(CD_3)_2SO$.

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