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LETTERS TO THE EDITOR

Non-Catalytic Alkylation of Aniline with 1,3,5-Trimethyl-4-hydroxymethylpyrazole

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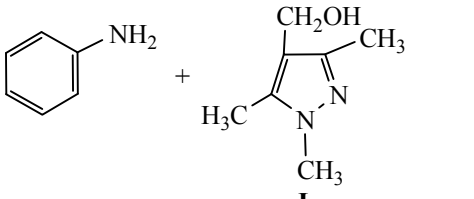
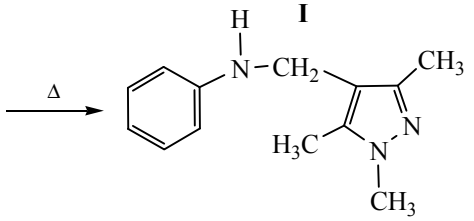
The electron density in the benzene ring, preferably in the *ortho*- and *para*-positions, is known to be increased in benzenes containing activating groups as substituents. For this reason, the reaction of electrophilic substitution in anilines, phenols, alkylbenzenes, and related derivatives occurs in the *ortho*- and *para*-positions of the ring [1]. As it was shown earlier [2], the noncatalytic alkylation of phenol with 1,3,5-trimethyl-4-hydroxymethylpyrazole **I** proceeded similarly to give *C*-alkylation products as a mixture of *ortho*-and *para*-isomers with a yield of 67%.

We suggested that the alkylation of aniline with 1,3,5-trimethyl-4-hydroxymethylpyrazole **I** should also lead to the formation of *ortho*- and *para*-alkylated products. However, in this case the electrophilic substitution in the benzene ring was found not to occur. The *N*-alkylation product **II** was isolated and characterized instead of *C*-alkylation products.

The structure of compound **II** was confirmed by the IR, ^{1}H and ^{13}C NMR spectroscopy and its composition, by the elemental analysis data.



I



II

***N*-(1,3,5-Trimethyl-1*H*-pyrazol-4-yl)methylaniline (II).** A mixture of 6.0 g of 4-hydroxymethyl-1,3,5-trimethylpyrazole **I** and 65 g of aniline was refluxed for 10 h. Aniline excess was removed, to the residue 10 ml of water and 100 ml of diethyl ether was added. The organic layer was separated, dried over $MgSO_4$, and evaporated. The residue was distilled in a vacuum. Yield 5.0 g (54%), bp 190–192°C (1 mm Hg), mp 95–100°C (isopropanol). IR spectrum, ν, cm^{-1}: 1550 (pyrazole), 1600 (phenyl), 3300 (NH). ^{1}H NMR spectrum, δ, ppm: 2.12 s (3H, 3-CH_3), 2.22 s (3H, 5-CH_3), 3.66 s (3H, N-CH_3), 3.89 br. s (2H, CH_2), 4.78 br.s (1H, NH), 6.51 t.t (1H, H^4, C_6H_5, ^3J 7.3, ^4J 1.1 Hz), 6.56 m (2H, H^{2,6}, C_6H_5), 7.03 m (2H, H^{3,5}, C_6H_5). ^{13}C NMR spectrum, δ_C, ppm: 9.0 and 11.2 (3,5-CH_3), 35.0 (1-CH_3), 37.1 (CH_2), 111.8 (C^{2,6}, C_6H_5), 112.8 (C^4, pyrazole), 115.5 (C^4, C_6H_5), 128.2 (C^{3,5}, C_6H_5), 136.2 (C^1, C_6H_5), 144.6 and 148.4 (C^{3,5}, pyrazole). Found, %: C 72.18; H 7.31; N 19.85. $C_{13}H_{17}N_3$. Calculated, %: C 72.55; H 7.90; N 19.53.

The IR spectra were registered on a Specord 75 IR spectrophotometer from thin film. The ^{1}H and ^{13}C NMR spectra were recorded on a Varian Mercury-300 instrument (300 MHz) in DMSO-d_6.

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