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LETTERS TO THE EDITOR

Non-catalytic Alkylation of Benzylamine with 1,3,5-Trimethyl-1*H*-pyrazol-4-ylmethanol

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We previously showed [1] that non-catalytic alkylation of aniline with 1,3,5-trimethyl-1*H*-pyrazol-4-ylmethanol (I) involves the nitrogen atom of aniline with formation of the corresponding *N*-pyrazolylmethyl derivative, whereas no C-alkylated derivative was isolated. We presumed that the alkyla-tion of benzylamine with 1,3,5-trimethyl-1*H*-pyrazol-4-ylmethanol (I) should also lead N-alkylation product. The reaction was carried out by heating com-pound I with a large excess of benzylamine at the boiling point in the absence of solvent and catalyst. As a result, instead of the expected N-(pyrazolylmethyl)-benzylamine II, from the reaction mixture, by vacuum distillation, we isolated dipyrazolylmethane (IV) and



N-benzylidenebenzylamine (**VII**). The formation path of bis(1,3,5-trimethyl-1*H*-pyrazol-4-yl)methane (**IV**) was studied by us in detail in [2].

Thus we have shown that compound I in the reaction with benzylamine acts as a source of formaldehyde [2] rather than as alkylating agent (in contrary to the reactions with phenol and aniline [1, 3]). Formaldehyde generated *in situ* reacts with benzylamine to produce intermediate *N*-methylidenebenzylamine (V), triadic prototropic rearrangement of the latter yields *N*-benzylidenemethanamine (VI) [4], and the final amine exchange reaction between VI and benzylamine leads to compound VII via elimination of methanamine.

The structure of **VII** was confirmed by the IR and ¹H NMR data. The IR spectrum of **VII** characteristically contained absorption bands due to stretching vibrations of the HC=N bond at 1640 cm⁻¹ and benzene ring at 1500–1600 cm⁻¹. In the ¹H NMR spectrum of **VII**, the CH₂ group gave a signal at δ 4.82 ppm, the HC=N proton resonated in a weak field (δ 8.40 ppm), and aromatic proton signals were observed in the region δ 7.2–7.82 ppm.

N-Benzylidenebenzylamine (VII) and bis(1,3,5trimethyl-1*H*-pyrazol-4-yl)methane (IV). A mixture of 43 g of benzylamine and 6 g of 1,3,5-trimethyl-1*H*pyrazol-4-ylmethanol (I) was heated for 4–5 h under reflux. After removal of excess benzylamine, the residues was distilled under reduced pressure to isolate 1.5 g (64%) of compound **VII** with bp 140°C (2 mm), $n_D^{20} = 1.600$ [5]. ¹H NMR spectrum, δ , ppm: 4.78 d (2H, CH₂, J = 1.3), 7.17–7.32 m (5H, C₆H₅), 7.37–7.42 m (3H, Ph), 7.73–7.78 m (2H, Ph), 8.40 t (1H, N=CH, J = 1.3). Found, %: C 86.45; H 6.20; N 7.43. C₁₄H₁₃N. Calculated, %: C 86.15; H 6.66; N 7.07. In addition, 2.3 g (50%) of dipyrazolylmethane **IV** [2] was isolated from the reaction mixture; mp 87°C (from petroleum ether).

The IR spectra were recorded on a Specord 75 IR spectrometer from thin films. The ¹H NMR spectra were measured on a Varian Mercury-300 instrument at 300 MHz using DMSO- d_6 as solvent.

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