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LETTERS TO THE EDITOR

REACTION OF 1-METHYL-4-NITROPYRAZOLE WITH 4-AMINO-1,2,4-TRIAZOLE

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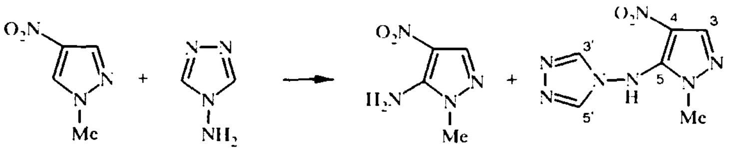
Earlier [1] we realized the vicarious C-amination of 1-methyl-4-nitropyrazole (**1**) by the action of 1,1,1-trimethylhydrazinium halides. The yield of the amination product 5-amino-1-methyl-4-nitropyrazole (**2**) amounted to 15-20%. While continuing these investigations we used as aminating agent 4-amino-1,2,4-triazole (**3**), which has been used successfully in reaction with nitrobenzene. As a result of this reaction *p*-nitroaniline was obtained with a yield of 58% [2].

We studied the reaction of 1-methyl-4-nitropyrazole **1** with 4-amino-1,2,4-triazole in absolute DMSO at 20°C in the presence of potassium *tert*-butoxide. The reaction led to a mixture of products, from which by fractional crystallization we isolated 1-methyl-4-nitropyrazol-5-yl(1,2,4-triazol-4-yl)amine (**4**) with a yield of 13% in addition to compound **2** (yield 20%).



1 **3** **2** **4**

During an attempt to conduct the reaction of compounds **1** and **3** with an equimolar ratio of the reagents at 20°C in a superbasic medium (DMSO/KOH) we only isolated the initial 1-methyl-4-nitropyrazole **1**.

5-Amino-1-methyl-4-nitropyrazole (2) and 1-Methyl-4-nitropyrazol-5-yl(1,2,4-triazol-4-yl)amine (4). To a solution of 1-methyl-4-nitropyrazole **1** (2.5 g, 0.02 mol) in absolute DMSO (30 ml) we added 4-amino-1,2,4-triazole **3**. The mixture was stirred at 20°C until the reagents had completely dissolved, and potassium *tert*-butoxide (5.3 g, 0.048 mol) was added. A red-black color was observed. The solution was stirred at 20°C for 10 h, the reaction mixture was poured onto ice, the mixture was acidified to pH ~ 5.0 with 10% hydrochloric acid, and the product was extracted three times with ethyl acetate. The extracts were washed with water and dried with sodium sulfate. The solvent was evaporated to dryness under vacuum, the residue was dissolved in acetone, and the insoluble part was filtered off. The acetone solution was partly evaporated and cooled to 0°C. The precipitate was filtered off and recrystallized from a 1:1 mixture of methanol and acetonitrile and then from water. We obtained 0.82 g (20%) of compound **2**; mp 265-266°C. ^{1}H NMR spectrum (DMSO-d_6), ppm: 3.56 (3H, s, CH_3);

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7.38 (2H, s, NH_2); 7.84 (1H, s, $C_{(3)}H$). ^{13}C NMR spectrum (DMSO-d_6), ppm: 35.04 (CH_3); 117.84 ($C_{(4)}$); 134.37 ($C_{(3)}$); 146.01 ($C_{(5)}$). ^{15}N NMR spectrum (DMSO-d_6), ppm: 80.5 (NO_2); 92.1 ($N_{(2)}$); 207.2 (NCH_3); 316.9 (NH_2). Found, %: C 33.86; H 4.36; N 39.28. $C_4H_6N_4O_2$. Calculated, %: C 33.80; H 4.22; N 39.43.

The crystalline residue insoluble in acetone was recrystallized from DMF. We obtained 0.35 g (13%) of compound **4**; mp 224-225°C. IR spectrum (KBr), cm^{-1}: 3120 (ν NH); 1620, 1490 (ν NO_2); 1580 (ν C=N); 1360 (δ CH_3). ^1H NMR spectrum (DMSO-d_6), ppm: 3.46 (3H, s, CH_3); 7.12 (1H, s, CH of pyrazole ring); 8.51 (2H, s, 2CH of triazole ring); 14.1 (1H, s, NH). ^{13}C NMR spectrum (DMSO-d_6), ppm: 34.02 (CH_3); 128.39 ($C_{(3)}$); 139.24 ($C_{(3')}$; $C_{(5')}$); 146.20 ($C_{(4)}$); 155.04 ($C_{(5)}$). Found, %: C 36.51; H 3.72; N 42.76. $C_6H_7N_7O_2$. Calculated, %: C 36.92; H 3.58; N 43.07.

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