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LETTERS TO THE EDITOR

Synthesis and Crystal Structure of 3-{(2-Carboxyethyl)-[2-(3-methylpyrazol-1-yl)-ethyl]amino}- and 3-{(2-Carboxyethyl)[2-(5- methylpyrazol-1-yl)-ethyl]amino} Propionic Acids

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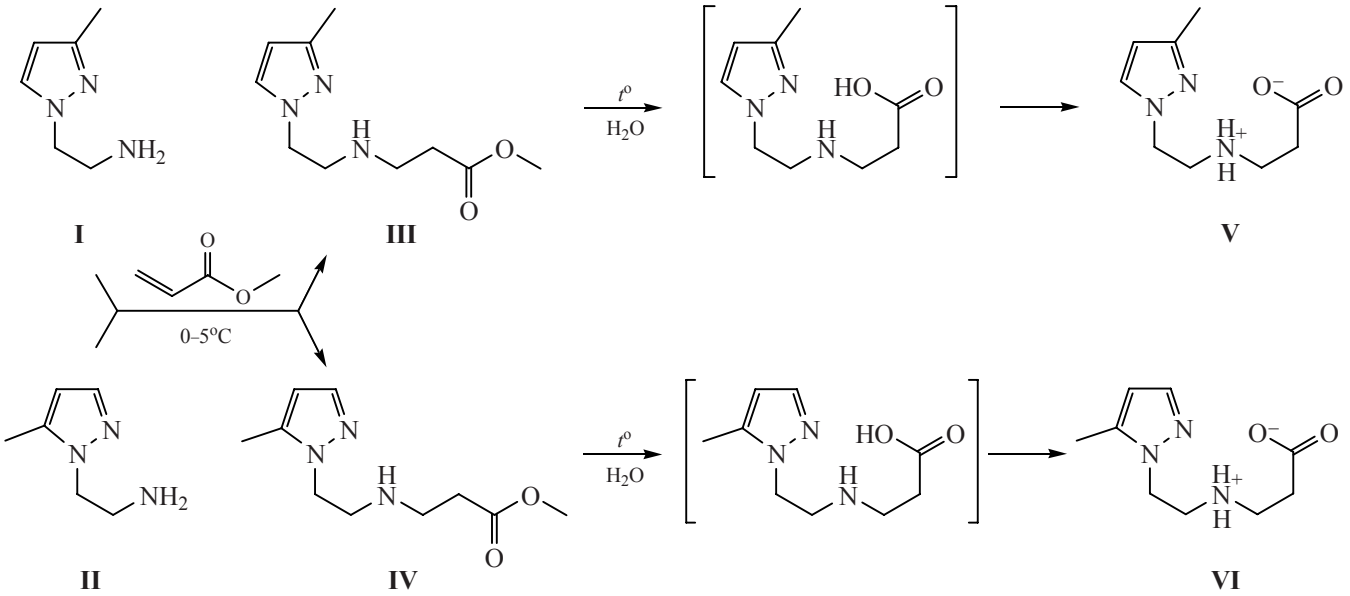
We have found that 1(β-aminoethyl)-3-methyl- and 1-(β-aminoethyl)-5-methylpyrazoles (**I, II**) easily add to methyl acrylate. The structure and composition of the products **III, IV** was confirmed by the ^{1}H NMR spectra and the elemental analysis data (Scheme 1).

As known, esters including the pyrazole-containing ones [1–4] are hydrolyzed in the presence of acids or bases. It was found that compounds **III, IV** are partially hydrolyzed during distillation evidently due to the specific intramolecular basic catalysis with the participation of NH group of the aliphatic chain [5].

It was established by means of the X-ray study by an example of substance **V** that compounds obtained **V, VI** exist exclusively as salts.

3-[2-(3-Methylpyrazol-1-yl)ethylamino] propionic acid (V). 1-(β-Aminoethyl)-3-methylpyrazole **I**, 12.5 g,

Scheme 1.



was cooled to 5–10°C, and 25.8 g of methyl acrylate was added dropwise. The resulting mixture was left at room temperature for a day. Excess methyl acrylate was removed at reduced pressure, and the residue was distilled in a vacuum to give 15.3 g of the product with bp 135–160°C (1 mm Hg). According to ^{1}H NMR spectrum the ratio of compounds **III, V** was 9:1. The distillate obtained was treated with 50 ml of 2-propanol and left overnight. The crystals of compound **V** were filtered off. Yield of the product 1.4 g, mp 173°C (from 2-propanol). IR spectrum, ν, cm^{-1}: 1540 (pyrazole ring), 1670 (C=O). ^{1}H NMR spectrum (300 MHz, DMSO-d_6), δ, ppm (*J*, Hz): 2.14 s (3H, CH_3), 2.29 t (2H, CH_2CO, *J* 6.6), 2.74 t (2H, NHCH_2CH$_2$CO, *J* 6.6), 2.91 t (2H, NHCH_2CH$_2$Ar, *J* 6.3), 4.08 t (2H, CH_2Ar, *J* 6.3), 4.36 br.s (2H, NH and COOH), 5.97 d (1H, 4-H_{pyr}, *J* 2.2), 7.55 d (1H, 5-H_{pyr}, *J* 2.2). Found, %: C 54.56, H 7.83, N 21.89. $C_9H_{15}N_3O_2$. Calculated, %: C 54.82, H 7.61, N 21.32.

3-[2-(5-Methylpyrazol-1-yl)ethylamino] propionic acid (VI). This compound was prepared analogously to the previous case from 12.5 g of compound **II**. Yield of distillate 15.9 g, [bp 140–165°C (1 mm Hg), ratio of compounds **IV** : **VI** = 9 : 1]. Yield of compound **VI** 1.6 g, mp 178°C (from 2-propanol). IR spectrum, ν, cm^{-1}: 1550 (pyrazole ring), 1670 (C=O). ^{1}H NMR spectrum (300 MHz, DMSO-d_6) δ, ppm (*J*, Hz): 2.25 s (3H, CH_3), 2.30 t (2H, CH_2CO, *J* 6.6), 2.76 t (2H, NHCH_2CH$_2$CO, *J* 6.6), 2.93 t (2H, NHCH_2CH$_2$Ar, *J* 6.4), 4.08 t (2H, CH_2Ar, *J* 6.4), 4.64 br.s (2H, NH and COOH), 5.99 d (1H, 4-H_{pyr}, *J* 1.9), 7.29 d (1H, 3-H_{pyr}, *J* 1.9). Found, %: C 54.31, H 7.72, N 22.16. $C_9H_{15}N_3O_2$. Calculated, %: C 54.82, H 7.61, N 21.32.

IR spectra were obtained on a UR-20 spectrometer from thin films. ^{1}H NMR spectra were taken on a Varian Mercury 300 spectrometer.

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