AN INVESTIGATION OF PYRAZOLES

LVII. Synthesis of 1- and 4-Vinylpyrazoles*

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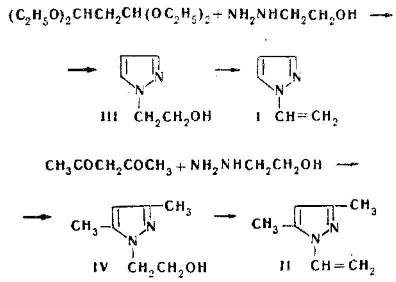
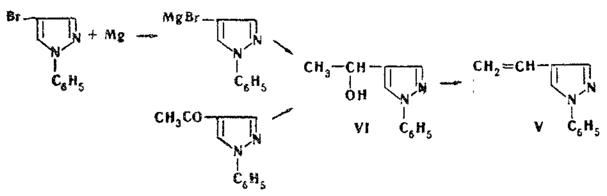
Methods have been developed for obtaining vinyl derivatives of various pyrazoles containing vinyl groups in positions 1 and 4 from the corresponding hydroxyethyl derivatives.

Recently, ever-increasing attention has been devoted to the synthesis of vinyl compounds of nitrogen heterocycles, some of which have found use as additives in the production of synthetic rubbers [2, 3]. The synthesis of 3,5-dimethyl-1-vinylpyrazole by the reaction of 3,5-dimethylpyrazole with acetylene under pressure in the presence of a catalyst has been reported [4].

We have obtained 1-vinylpyrazole (I) and 3,5-dimethyl-1-vinylpyrazole (II) by dehydrating the corresponding alcohol, 1-(β-hydroxyethyl)pyrazole (III) and 3,5-dimethyl-1-(β-hydroxyethyl)pyrazole (IV). The alcohols were obtained by condensing tetraethoxypropane and acetylacetone with β-hydroxyethylhydrazine.



We have synthesized 1-phenyl-4-vinylpyrazole (V), obtained previously [5] by the decarboxylation of β-(1-phenyl-4-pyrazolyl)acrylic acid, from 1-(1'-phenyl-4'-pyrazolyl)ethanol (VI), obtained by the Grignard reaction from 4-bromo-1-phenylpyrazole and by reduction of the readily-accessible 1-phenyl-4-acetylpyrazole [6]. The alcohol itself was not isolated in the pure state because of the extreme readiness of its dehydration to 1-phenyl-4-vinylpyrazole.



EXPERIMENTAL

β-Hydroxyethylhydrazine. Over 4 hr, 44 g (1 mole) of ethylene oxide was slowly bubbled into 212 ml of a 50% solution of hydrazine hydrate at 10°–15° C, and the mixture was left overnight. After the water and hydrazine hydrate had been driven off from the reaction mixture in vacuum, the β-hydroxyethylhydrazine was distilled off from the residue. Yield 43 g (57%), bp 123°–124° C (11 mm); n_D^{20} 1.4890 [7].

1-(β-Hydroxyethyl)pyrazole (III). A solution of 14.8 g (0.2 mole) of β-hydroxyethylhydrazine in 30 ml of ethanol and 50 ml of water was treated with 35 ml of hydrochloric acid (1 : 1) and then, at 40°–50° C, with stirring, 44 g (0.2 mole) of tetraethoxypropane was added dropwise. The reaction mixture was boiled for an hour and left overnight. After the ethanol had been distilled off, the mixture was made alkaline with an excess of potassium carbonate and carefully extracted with chloroform. The extract was dried with magnesium sulfate and distilled in vacuum. This gave 13.2 g (60%) of III with bp 82°–83° C (2 mm); n_D^{20} 1.5030, d_4^{20} 1.1225, R_f 0.55 (Al_2O_3 of activity grade II, ethyl acetate—ethanol, 9 : 1). Found, %: C 53.23, 53.18, H 7.45, 7.35. Calculated for $C_5H_8N_2O$, %: C 53.55; H 71.9. **Picrate:** mp 118°–119° C (from aqueous methanol). Found, %: C 38.40, 38.30; H 3.27, 3.24. Calculated for $C_5H_8N_2O \cdot C_6H_3N_3O_7$, %: C 38.72; H 3.25.

3,5-Dimethyl-1-(β-hydroxyethyl)pyrazole (IV). With cooling to 10° C, 8 g (0.08 mole) of acetylacetone was added to a solution of 6.1 g (0.08 mole) of β-hydroxyethylhydrazine in 20 ml of methanol. The reaction mixture was stirred for an hour, heated to the boil under reflux, and left overnight. After the methanol had been distilled off in vacuum, the residue was crystallized from heptane. This gave 9.9 g (88%) of IV with mp 77° C, readily subliming. R_f 0.56 (Al_2O_3 of activity grade II, ethyl acetate—ethanol, 9 : 1). Found, %: C 60.40, 60.30; H 8.93, 8.83. Calculated for $C_7H_{12}N_2O$, %: C 59.97; H 8.63. **Picrate:** mp 105°–106° C (from aqueous methanol). Found, %: C 42.36, 42.24; H 4.16, 4.05. Calculated for $C_7H_{12}N_2O \cdot C_6H_3N_3O_7$, %: C 42.28; H 4.09.

1-Vinylpyrazole (I). A mixture of 5.6 g (0.05 mole) of 1-(β-hydroxyethyl)-pyrazole and 2.5 g (0.045 mole) of powdered potassium hydroxide was heated in a Wurtz flask in a metal bath to 230° C. At 200°–220° C, 1-vinylpyrazole and water passed over. The distillate was treated with 0.5 g of fused potassium hydroxide and the vinylpyrazole layer was separated off, dried with potassium hydroxide, and redistilled in vacuum. This gave 2.4 g (50%) of I with bp 62° C (52 mm); n_D^{20} 1.5162, d_4^{20} 1.0026, R_f 0.73, (Al_2O_3 of activity grade II, chloroform). UV spectrum (SF-4, methanol): λ_{max} 247 nm, log ε 4.08.

3,5-Dimethyl-1-vinylpyrazole (II) was obtained similarly from the alcohol IV with a yield of 64%, bp 67°–68° C (11 mm), n_D^{20} 1.5161, d_4^{20} 0.9625, R_f 0.72 (Al_2O_3, activity grade II, chloroform). Found, %: C 68.41, 68.36; H 8.18, 8.17. Calculated for $C_7H_{10}N_2$, %: C 68.82; H 8.25; UV spectrum (SF-4, methanol), λ_{max} 253 nm, log ε 4.06. **Picrate:** mp 87° C (from absolute ethanol). Found, %: C 44.71, 44.61; H 4.00, 3.85. Calculated for $C_7H_{10}N_2 \cdot C_6H_3N_3O_7$, %: C 44.45; H 3.73.

1-Phenyl-4-vinylpyrazole (V). a) A three-necked flask with a stirrer, dropping funnel, and reflux condenser was filled with 7.2 g (0.3 g-atom) of metallic magnesium and 30 ml of dry ether. A mixture of 33.8 g (0.18 mole) of ethylene bromide and 13.4 g (0.06 mole) of 4-bromo-1-phenylpyrazole (mp 80°–81° C [8]) in 100 ml of dry ether was added very slowly (one drop in 3 sec) to the magnesium. The reaction mixture was heated to a boil for half an hour and, after cooling with ice, 5.3 g (0.12 mole) of freshly-distilled acetaldehyde in 15 ml of dry ether was added. The mixture was decomposed with 2 N HCl. The ethereal layer was separated off and the aqueous layer extracted with chloroform. The extracts, combined with

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*For communication LVI, see [1].

the ethereal layer, were dried with magnesium sulfate, the solvent was driven off, and the residue was distilled in vacuum. This yielded 5 g (48%) of V with bp 123°–128° C (2 mm) in the form of a viscous liquid which rapidly crystallized. Mp 39°–40° C (from petroleum ether).

b) One gram of Raney nickel was added to a solution of 1.86 g (0.01 mole) of 4-acetyl-1-phenylpyrazole (mp 127° C [6]) in 100 ml of ethanol, and the mixture was shaken at room temperature in an atmosphere of hydrogen for 30 hr. The nickel was filtered off. After the ethanol had been driven off and the residue had been distilled in vacuum, 1.26 g (75%) of V was obtained with bp 129°–131° C (4 mm), mp 39°–40° C (from petroleum ether). R_f 0.77 (Al_2O_3 of activity grade II, chloroform). Found, %: C 77.40, 77.35; H 5.82, 5.79. Calculated for $C_{11}H_{10}N_2$, %: C 77.61; H 5.92. UV spectrum (SF-4, methanol): λ_{max} 274 nm, log ε 4.15.

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