

SHORT
COMMUNICATIONS

Reaction of 3(5)-Methylpyrazole with Vinyl Acetate in the Presence of Mercury Acetate

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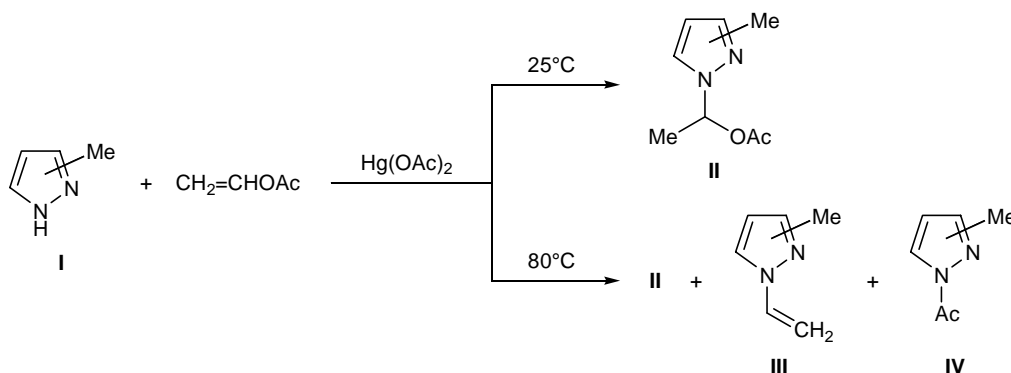
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It is known that mercury(II) acetate in the presence of strong acids (e.g., H_2SO_4) catalyzes vinyl exchange reaction between vinyl esters (such as vinyl acetate) and NH-heterocycles [1–4]. We have found that 3(5)-methylpyrazole (**I**) reacts with vinyl acetate in the presence of a catalytic amount of mercury(II) acetate at room temperature without addition of sulfuric acid to give addition product **II** in 80% yield. When the reaction was performed at elevated temperature (80°C), apart from compound **II**, a mixture of 1-vinyl-3(5)-methylpyrazole (**III**) and 1-acetyl-3(5)-methylpyrazole (**IV**) was formed in an overall yield of 30% (ratio 1:3). In the presence of a catalytic amount of sulfuric acid (but without mercury catalyst), the only product was *N*-acetylpyrazole **IV** (yield 40%).

1-(1-Acetoxyethyl)-3(5)-methylpyrazole (II). Mercury(II) acetate, 1 g, was added to a mixture of 0.1 mol of 3(5)-methylpyrazole (**I**) and 50 ml of vinyl acetate, and the mixture was left to stand for 12 h at room temperature. Sodium acetate, 3.0 g, was then added to decompose the mercury catalyst, the mixture was kept for 2 h, the precipitate was filtered off, and the filtrate was neutralized with a 2 N solution of sodium carbonate and extracted with diethyl ether. The

extract was dried over magnesium sulfate and evaporated, and the residue was distilled under reduced pressure. Yield 72%, bp $75\text{--}80^\circ\text{C}$ (2 mm), $n_D^{20} = 1.4738$. IR spectrum, ν , cm^{-1} : 1520 (pyrazole ring), 1740 (C=O). ^1H NMR spectrum (DMSO- d_6 , 300 MHz), δ , ppm: 1.80 d (3H, CHCH_3 , $J = 6.2$ Hz), 2.05 s (3H, CH_3CO), 2.25 s [3H, 3(5)- CH_3], 5.95 d (1H, 4-H, $J = 2.3$ Hz), 6.65 q (1H, NCH, $J = 6.2$ Hz), 7.55 d [1H, 3(5)-H, $J = 2.3$ Hz]. Found, %: C 57.17; H 7.12; N 16.30. $\text{C}_8\text{H}_{12}\text{N}_2\text{O}_2$. Calculated, %: C 57.14; H 7.14; N 16.67.

3(5)-Methyl-1-vinylpyrazole (III). A mixture of 0.1 mol of 3(5)-methylpyrazole (**I**), 50 ml of vinyl acetate, 1.0 g of mercury(II) acetate, and a few crystals of hydroquinone was stirred for 6 h at $70\text{--}80^\circ\text{C}$. Sodium acetate, 3.0 g, was then added to decompose the mercury catalyst, the mixture was kept for 2 h, the precipitate was filtered off, and the filtrate was neutralized with a 2 N solution of sodium carbonate and extracted with diethyl ether. The extract was dried over magnesium sulfate and evaporated, and the residue was distilled under reduced pressure. Yield 8%, bp $55\text{--}60^\circ\text{C}$ (10 mm), $n_D^{20} = 1.5160$. IR spectrum, ν , cm^{-1} : 1530 (pyrazole ring). ^1H NMR spectrum (DMSO- d_6 , 300 MHz), δ , ppm: 2.17 s [3H, 3(5)- CH_3],



4.76 d.d (1H, =CH₂, $J = 9.3, 1.5$ Hz), 5.42 d.d (1H, =CH₂, $J = 15.7, 1.5$ Hz), 5.85 d (1H, 4-H, $J = 2.0$ Hz), 6.92 d.d (1H, NCH, $J = 15.7, 9.3$ Hz), 7.32 d [1H, 3(5)-H, $J = 2.3$ Hz]. Found, %: C 66.70; H 7.38; N 25.91. C₆H₈N₂. Calculated, %: C 66.67; H 7.41; N 25.93.

1-Acetyl-3(5)-methylpyrazole (IV). A mixture of 0.1 mol of 3(5)-methylpyrazole (I), 50 ml of vinyl acetate, and 0.12 ml of sulfuric acid was heated for 6 h at 70–80°C. The mixture was then neutralized with a 2 N solution of sodium hydroxide and extracted with diethyl ether, the extract was dried over magnesium sulfate, and evaporated, and the residue was distilled under reduced pressure. Yield 40%, bp 90–100°C (35 mm), $n_D^{20} = 1.4610$. IR spectrum, ν , cm⁻¹: 1530 (pyrazole ring), 1700 (C=O). ¹H NMR spectrum (DMSO-*d*₆, 300 MHz), δ , ppm: 2.30 s [3H, 3(5)-CH₃], 2.62 s (3H, CH₃CO), 6.25 d (1H, 4-H, $J = 2.3$ Hz), 8.13 d [1H, 3(5)-H, $J = 2.3$ Hz]. Found, %: C 58.09; H 6.42; N 22.30. C₆H₈N₂O. Calculated, %: C 58.06; H 6.45; N 22.58.

The IR spectra were recorded on a UR-20 spectrometer from samples prepared as thin films or KBr pellets. The ¹H NMR spectra were obtained on a Varian Mercury-300 spectrometer using HMDS as internal reference. GLC analysis was performed on an LKhM-8MD chromatograph equipped with a 1-m column; stationary phase 10% of Carbowax-20M on Inerton AW-HMDS; carrier gas helium, flow rate 40 ml/min; detector temperature 220°C.

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