

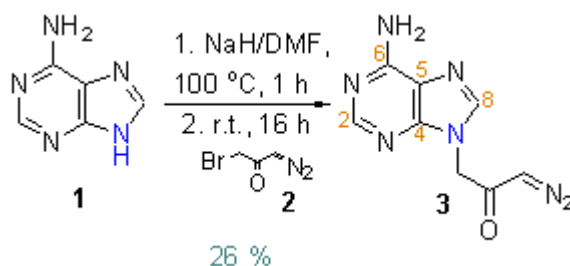
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1-(6-Amino-9H-purin-9-yl)-3-diazoacetone

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Adenine (**1**, 0.676 g, 5.0 mmol) was suspended in anhydrous DMF (20 mL) and sodium hydride (55-60 % suspension in mineral oil, 0.262 g, 6.0 mmol) was added at room temperature. The mixture was vigorously stirred at 100 °C for 1 h and then cooled to room temperature. 1-Bromo-3-diazo-propan-2-one (**2** [1,2], 0.978 g, 6.0 mmol) was added dropwise at this temperature. The reaction mixture immediately turned brown and the initial sodium adenide dissolved. The mixture was set aside at room temperature. After 16 h t.l.c. (20 % v/v methanol in dichloromethane) indicated that the reaction mixture still contained significant amounts of unreacted adenine. After evaporating the solvent *in vacuo* the residue was successively coevaporated with toluene (2 x) and ethanol (2 x). Chromatographic purification (5-8 % v/v methanol in dichloromethane) afforded the product (**3**, 0.280 g, 26 %). An analytical sample was obtained by recrystallization from methanol. Attempts to improve the yield using different bases (sodium ethylate or potassium carbonate), reaction times or temperatures (0 °C to 100 °C) failed. T.l.c. showed that compound **3** is not indefinitely stable in the reaction mixture. Adenine is known to react with alkylating agents under basic conditions to give *N*⁹-substituted derivatives [3].

Yield: 26 %.

Mp.: 187-189 °C (dec.).

IR (KBr): 1334m ($\nu_{\text{C}=\text{N}=\text{N}}$); 1644s; 1658s ($\nu_{\text{C}=\text{O}}$); 2110s ($\nu_{\text{as}}\text{C}=\text{N}=\text{N}$).

¹H NMR (DMSO-*d*₆, 400 MHz): 5.03 (s, 2 H, CH₂N); 6.18 (s, 1 H, CHN₂); 7.25 (br s, 2 H, NH₂); 8.08 (s, 1 H, H-2*); 8.12 (s, 1 H, H-8*).

¹³C NMR (DMSO-*d*₆, 100 MHz, assignment based on *J*-modulated spin-echo experiment): 48.98 (CH₂N); 53.77 (CHN₂); 118.29 (C-5); 141.46 (C-8); 149.68 (C-4); 152.56 (C-2); 155.93 (C-6); 188.43 (CO).

EI-MS (NH₄Cl additive, *m/z*, %): 217 (3, M⁺); 189 (100, [M-28]⁺); 160 (23); 148 (18); 135 (48, [adenine]⁺); 108 (35, [adenine-HCN]⁺); 55 (80, C₃H₃O⁺).

Anal calcd. for C₈H₇N₇O (217.188): C, 44.24; H, 3.25; N, 45.14; found C, 44.06; H, 3.02; N, 45.15 %.

References

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Sample availability: sample available from the author.

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