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AN ORIGINAL APPROACH TO THE SYNTHESIS OF THE BENZO[*g*]INDAZOLE HETEROCYCLIC SYSTEM

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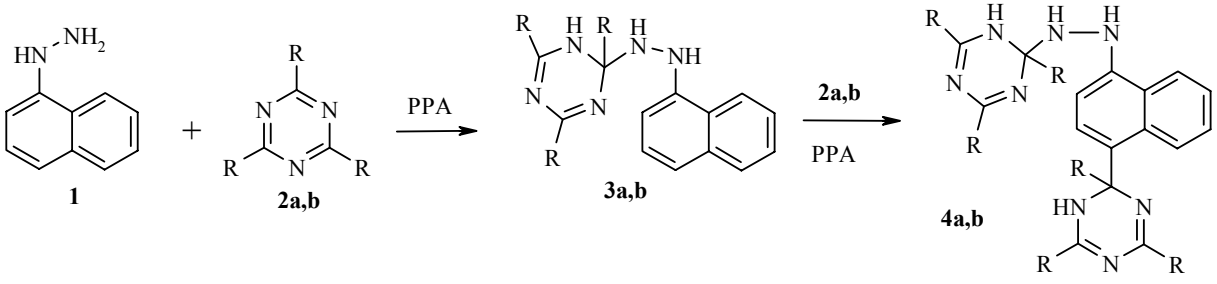
Hydrazines are known to react with 1,3,5-triazines **2** to give triazoles [1, 2]. We undertook a study to determine whether the regioselectiv of this reaction is altered upon going to trazines **2** in polyphosphoric acid (PPA). We unexpectedly found that the reaction of 1 mmol 1-naphthylhydrazine (**1**) with 2.5 mmol compound **2a** in 3-4 g PPA*, initially at 65-70°C for 2 h and then at 110-120°C for 3 h leads to previously unreported 1H-benzo[*g*]indazole-5-carbaldehyde (**6a**) in 82% yield. The isolation of the product was the same as for similar reactions [3]. The reaction with 2,4,6-trimethyl-1,3,5-triazine (**2b**) gave ketone **6b**. This reaction probably proceeds through the following sequence of steps.

The first step leads to intermediates **3**, which then react with an additional molecule of triazines **2** to give compounds **4**, which undergo heterocyclization to yield dihydrotriazines **5**. The hydrolysis of **5** gives benzoindazoles **6**.



1 **2a,b** **3a,b** **4a,b**

The NMR spectra were taken on a Bruker AS-200 spectrometer at 200 MHz in DMSO-d_6 with TMS as the internal standard. The IR spectra were taken on a Pye Unicam 9512 spectrometer for KBr pellets. The mass spectra were taken on a MAT-311A mass spectrometer. The reaction course and purity of the products were monitored on Silufol UV-254 plates with ethyl acetate as the eluent. Column chromatography was carried out on L 40/100 silica gel with ethyl acetate as the eluent.

* A sample of PPA with 86% H_3PO_4 prepared according to Uhlig [4] was used.

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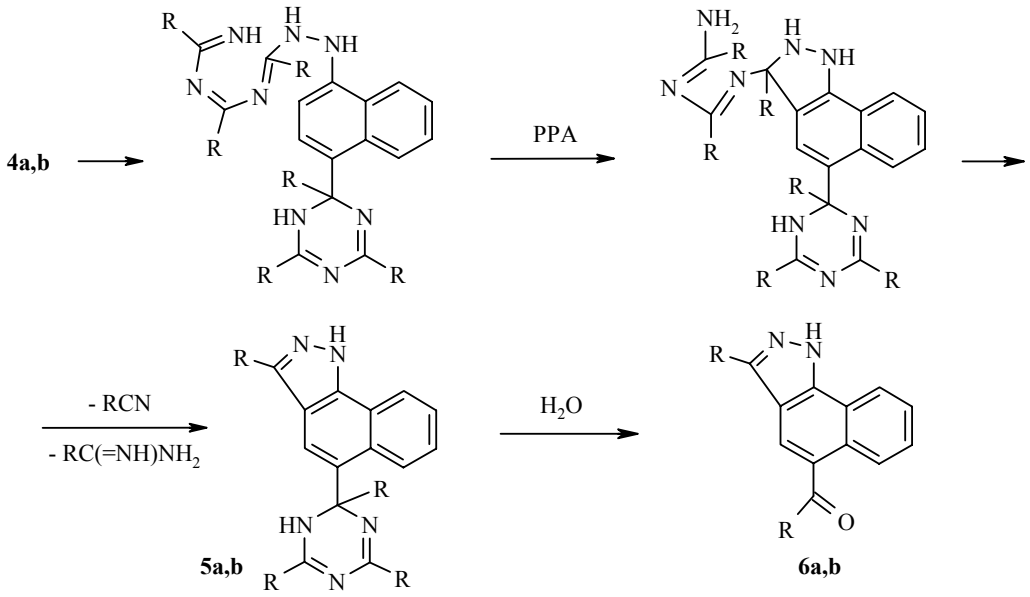

2–6 a R = H, **b** R = Me

1H-Benzo[*g*]indazole-5-carbaldehyde (6a) was obtained in 82% yield (0.161 g), mp 118-119°C (ethyl acetate). IR spectrum, ν, cm^{-1}: 1689 (C=O). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 7.41 (1H, d, *J* = 8.7, H-9); 7.62 (1H, dd, *J* = 8.7, *J* = 7.1, H-8); 7.82 (1H, dd, *J* = 8.0, *J* = 7.1, H-7); 7.84 (1H, s, H-3); 8.32 (1H, s, H-4); 8.74 (1H, d, *J* = 8.0, H-6); 9.88 (1H, s, CHO). Mass spectrum (70 eV), *m/z* (I_{rel}, %): 196 $[M]^+$ (71), 195 $[M-1]^+$ (100), 168 $[M-28]^+$ (84), 141 $[M-55]^+$ (100). Found, %: C 73.61; H 4.03; N 14.22. $C_{12}H_8N_2O$. Calculated, %: C 73.46; H, 4.11; N 14.28.

5-Acetyl-3-methyl-1H-benzo[*g*]indazole (6b) was obtained in 68% yield (0.152 g), mp 134-135°C (ethyl acetate). IR spectrum, ν, cm^{-1}: 1653 (C=O). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.92 (3H, s, CH_3CO); 2.83 (3H, s, CH_3); 7.37 (1H, d, *J* = 9.0, H-9); 7.64 (1H, dd, *J* = 9.0, *J* = 7.2, H-8); 7.81 (1H, dd, *J* = 8.0, *J* = 7.2, H-7); 7.99 (1H, d, *J* = 8.0, H-6); 8.18 (1H, s, H-4). Found, %: C 75.11; H 5.33; N 12.41. $C_{14}H_{12}N_2O$. Calculated, %: C 74.98; H 5.39; N 12.49.

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