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THERMAL CYCLIZATION OF 3-(1-NAPHTHYL)-1-PHENYLPYRAZOLE-4-CARBOXYLIC ACID IN POLYPHOSPHORIC ACID

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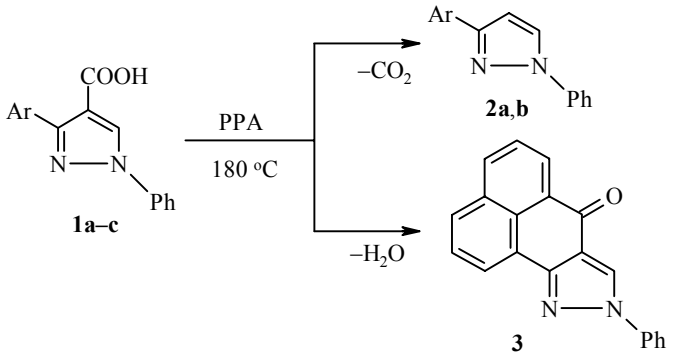
The thermal decarboxylation of pyrazole-4-carboxylic acids is used as a major method for the synthesis of pyrazoles unsubstituted at $C_{(4)}$ [1-3]. In particular, 1,3-diphenylpyrazole is obtained by heating 1,3-diphenyl-4-carboxylic acid in quinoline at reflux in the presence of copper powder [4].

We have found that 1,3-disubstituted pyrazole-4-carboxylic acids **1a** and **1b** are converted upon heating in polyphosphoric acid at 180°C to pyrazoles **2a** and **2b**. On the other hand, heating acid **1c**, which contains an α-naphthyl group at $C_{(3)}$ of the pyrazole ring, under analogous conditions leads not to decarboxylation, but rather intramolecular acylation to give a new heterocyclic system, phenalenopyrazole **3**, as the result of attack of the carboxylic acid group at $C_{(8)}$ in the naphthalene ring.



1, 2 a Ar = Ph, **b** Ar = 2-thienyl, **1c** Ar = 1-$C_{10}H_7$

The ^{1}H NMR spectra were taken on a Varian VXR-300 spectrometer at 300 MHz, DMSO-d_6. The IR spectrum was taken on a UR-20 spectrometer in a KBr pellet.

A sample of acid **1a-c** (0.005 mol) was added to polyphosphoric acid (50 g) obtained by dissolving P_2O_5 (25 g) in 85% phosphoric acid (25 g). The suspension was heated to 180°C and maintained at this temperature for 2 h, cooled, and poured onto 200 g of ice. The residue was filtered off, dried, and recrystallized.

1,3-Diphenylpyrazole (2a) was obtained in 69% yield; mp 83-84°C (ethanol) (mp 84°C [4]). ^{1}H NMR spectrum, δ, ppm, *J* (Hz): 8.57 (1H, d, *J* = 2.4, 5-H); 7.96-7.92 (4H, m, *o*-Ph); 7.56-7.33 (6H, m, *m*-, *p*-Ph); 7.05 (1H, d, *J* = 2.4, 4-H).

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1-Phenyl-3-(2-thienyl)pyrazole (2b) was obtained in 48% yield; mp 52-53°C (2:1 hexane–benzene). ^{1}H NMR spectrum, δ, ppm, *J* (Hz): 8.53 (1H, d, *J* = 2.7, 5-H); 7.87 (2H, d, *J* = 7.7, *o*-Ph); 7.60-7.43 (4H, m, *m*-, *p*-Ph, H thienyl); 7.30 (1H, t, *J* = 6.8, H thienyl); 7.12 (1H, m, H thienyl). 6.92 (1H, d, *J* = 2.7, 4-H). Found, %: C 69.29; H 4.42; N 12.24. $C_{13}H_{10}N_2S$. Calculated, %: C 69.00, H, 4.45; N 12.38.

4-Oxo-2-phenylphenaleno[2,3-*c*]pyrazole (3) was obtained in 76% yield; mp 243-245°C (dioxane). IR spectrum, ν, cm^{-1}: 1670 (C=O). ^{1}H NMR spectrum, δ, ppm, *J* (Hz): 9.33 (1H, s, 3-H); 8.58 (1H, d, *J* = 7.8, 7-H); 8.51 (1H, d, *J* = 7.8, 8-H); 8.38 (1H, d, *J* = 7.8, 5-H); 8.21 (1H, d, *J* = 7.8, 10-H); 8.11 (2H, d, *J* = 7.7, *o*-HPh); 7.83 (1H, t, *J* = 7.8, 6-H); 7.78 (1H, t, *J* = 7.8, 9-H); 7.60 (2H, m, *m*-HPh); 7.45 (1H, t, *J* = 7.7, *p*-HPh). Found, %: C 80.84; H 4.23; N 9.62. $C_{20}H_{12}N_2O$. Calculated, %: C 81.07; H 4.08; N 9.45.

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