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INTRAMOLECULAR CYCLIZATION OF 4-ISOCYANATO-3-(2-NAPHTHYL)-1-PHENYLPYRAZOLE UNDER FRIEDEL-CRAFTS REACTION CONDITIONS

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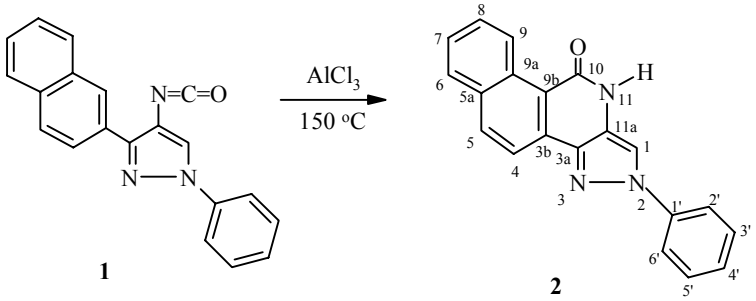
4-Isocyanato-3-(2-naphthyl)-1-phenylpyrazole cyclized under the influence of $AlCl_3$ to give 2H-benzo-[h]pyrazolo[4,3-c]isoquinoline.

Keywords: 2H-benzo[*h*]pyrazolo[4,3-*c*]isoquinoline, 4-isocyanatopyrazole, Friedel–Crafts reaction.

Isocyanates of a number of pyrazoles are a little studied type of heterylheterocumulenes. For example, there is only limited information about 3-isocyanatopyrazoles [1] and 4-isocyanatopyrazoles [2]. Recently [3] we reported the synthesis of the first examples of 3-aryl-4-isocyanato-1-phenylpyrazoles (Ar = Ph, 4-FC_6H_4, 4-ClC_6H_4, 4-BrC_6H_4, 4-EtC_6H_4) and their reactions with nucleophilic reagents. Our attempts to use these compounds for intramolecular cyclization with participation of the N=C=O group and the 3-aryl substituent were unsuccessful, although it had been shown [2] that cyclization of 5-isocyanato-4-ω-phenylalkylpyrazoles was possible under the influence of $AlCl_3$ to give 7-11 membered lactams, by condensation with the benzene and pyrazole rings.

We have chosen 4-isocyanato-3-(2-naphthyl)-1-phenylpyrazole (**1**) as a new compound which might undergo cyclization. It was synthesized by the use of the organosilicon variant [4] of the Curtius reaction with 3-(2-naphthyl)-1-phenylpyrazole-4-carbonyl chloride, which, in its turn, was obtained by oxidation of 4-formyl-3-(2-naphthyl)-1-phenylpyrazole.



1 **2**

On investigating the behavior of compound **1** under Friedel–Crafts conditions we observed an example of intramolecular carbamoylation by the isocyanato group at the α-position of the naphthalene ring to give a derivative 2H-benzo[*h*]pyrazolo[4,3-*c*]isoquinoline **2** (54% yield).

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The structure of compound **2** was confirmed by IR, ^{1}H and ^{13}C NMR spectroscopy. In particular there were characteristic bands for C=O (1680) and N–H (3180 cm^{-1}) of a lactam group in the IR spectrum. In the ^{1}H NMR spectrum the unique proton of the pyrazole ring appeared as two close singlets of approximately equal intensity, apparently caused by the conformational characterics of the pyridone ring.

EXPERIMENTAL

IR spectra were recorded on a UR-20 instrument. ^{1}H and ^{13}C NMR spectra were measured on a Varian VXR-300 instrument (at 300 and 75 MHz respectively) with TMS as internal standard.

4-Formyl-3-(2-naphthyl)-1-phenylpyrazole was prepared by a known method [5]. Yield 78%; mp 140-141°C (dioxane). IR spectrum (KBr), ν, cm^{-1}: 1695 (C=O). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 7.24-8.26 (12H, m , H arom); 8.47 (1H, s, 5-H); 10.02 (1H, s, CH=O). Found, %: C 80.85; H 5.07; N 9.57. $C_{20}H_{14}N_2O$. Calculated, %: C 80.51; H 4.73; N 9.39.

3-(2-Naphthyl)-1-phenylpyrazole-4-carboxylic Acid was obtained by a known method [6]. Yield 69%; mp 243-244°C. IR spectrum (KBr), ν, cm^{-1}: 1705 (C=O), 2600-2950 (COOH). ^{1}H NMR spectrum (acetone-d_6), δ, ppm: 7.23-8.31 (12H, m, H arom); 8.64 (1H, s, 5-H); 11.03 (1H, br. s, COOH). Found, %: C 76.11; H 4.52; N 9.23. $C_{20}H_{14}N_2O_2$. Calculated, %: C 76.42; H 4.49; N 8.91.

4-Isocyanato-3-(2-naphthyl)-1-phenylpyrazole (1). Thionyl chloride (0.72 ml, 10 mmol) and DMF (3-4 drops) were added to a suspension of 3-(2-naphthyl)-1-phenylpyrazole-4-carboxylic acid (1.57 g, 5 mmol) in anhydrous toluene (30 ml) and the mixture was boiled for 2 h. The toluene and excess thionyl chloride were evaporated from the mixture, toluene (15 ml) was added to the residue, then trimethylsilyl azide (0.69 g, 60 mmol) in toluene (5 ml) was added to the stirred and boiling mixture over 0.5 h. The mixture was heated for 4 h until evolution of nitrogen ceased. The solvent was evaporated and the residue was purified by crystallization from 3:1 benzene–hexane. Yield 76%; mp 132-134°C. IR spectrum (CH_2Cl_2), ν, cm^{-1}: 2270 (N=C=O). ^{1}H NMR spectrum (C_6D_6), δ, ppm: 6.85 (1H, s, 5-H); 7.04-8.36 (12H, m, H arom). Found, %: C 77.27; H 4.59; N 13.65. $C_{20}H_{13}N_3O$. Calculated, %: C 77.16; H 4.21; N 13.50.

2-Phenyl-2H-benzo[*h*]pyrazolo[4,3-*c*]isoquinolin-10(11H)-one (2). A solution of isocyanate **1** (0.5 g, 1.6 mmol) in *o*-dichlorobenzene (2 ml) was added to a suspension of $AlCl_3$ (0.45 g, 3.5 mmol) in *o*-dichlorobenzene (5 ml) heated to 80°C, the temperature was raised to 115°C and kept there for 1 h, then the temperature was rapidly raised to 150°C and heating was stopped. The solvent was evaporated from the cooled mixture, water (50 ml) was added to the residue, and the precipitate formed was filtered off and crystallized from dioxane. Yield 54%; mp 300°C. IR spectrum (KBr), ν, cm^{-1}: 1680 (C=O), 3180 (N–H). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 7.39-8.42 (11H, m, H arom); 10.18, 10.21 (1H, two s, 1-H); 11.71 (1H, s, NH). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 109.13 ($C_{(11a)}$), 117.03 ($C_{(2')}$ and $C_{(6')}$), 117.29 ($C_{(4)}$), 117.62 ($C_{(9b)}$), 122.58 ($C_{(3b)}$), 124.39 ($C_{(5)}$), 124.82 ($C_{(9)}$), 125.03 ($C_{(4')}$), 126.24 ($C_{(1)}$), 126.87 ($C_{(7)}$), 127.59 ($C_{(3')}$ and $C_{(5')}$), 129.17 ($C_{(9a)}$), 130.39 ($C_{(6)}$), 131.22 ($C_{(8)}$), 132.36 ($C_{(5a)}$), 134.66 ($C_{(1')}$), 138.06 ($C_{(3a)}$), 160.70 ($C_{(10)}$). Found, %: C 77.13; H 3.86; N 13.11. $C_{20}H_{13}N_3O$. Calculated, %: C 77.16; H 4.21; N 13.50.

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