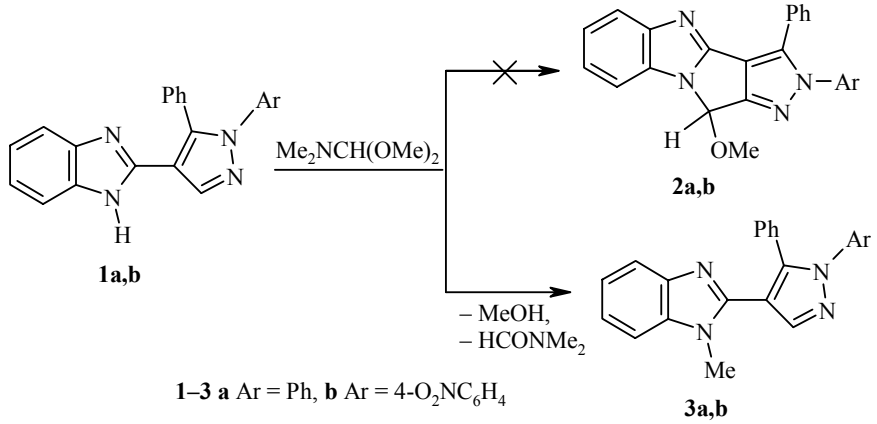
REACTION OF 2-(1-ARYL-5-PHENYLPYRAZOL-4-YL)-1H-BENZIMIDAZOLES WITH THE DIMETHYLACETAL OF DMF

I. B. Dzvinchuk and M. O. Lozinskii

Keywords: dimethyl acetal of DMF, 2-(4-pyrazolyl)benzimidazoles, N-methylation.

Previously [1] we assigned the structure **2a,b** to the products of the reaction of 2-(1-aryl-5-phenylpyrazol-4-yl)-1H-benzimidzoles **1a,b** with the dimethylacetal of DMF. This conclusion did not contradict the ^{1}H NMR spectral data, the elemental analysis, and information [2] on the existence of polycondensation of heterocyclic systems of this type. The result appeared to be unusual on the background of known [3-5] properties of the dimethylacetal of DMF.



1a,b

2a,b

3a,b

1–3 a Ar = Ph, **b** Ar = 4-$O_2NC_6H_4$

Over time, we had doubts about the correctness or our conclusions. We carried out additional chromato-mass–spectroscopic analysis and detected that the molecular mass did not coincide with that calculated for the structure **2a,b**. A second elemental analysis was carried out after thorough purification of the products. As a result it became evident that our original suggestion of the structure of the products was erroneous. In particular in the reaction cyclocondensation does not take place, but N-methylation at the benzimidazole nitrogen atom with formation of the compounds **3a,b**, which accords with the known properties of the dimethylacetal of DMF [5].

^{1}H NMR spectra of DMSO-d_6 solutions with TMS as the internal standard were recorded on a Varian VXR-300 (300 MHz) instrument. Chromatomass spectrometry was carried out on an Agilent 1100 series high resolution liquid chromatograph equipped with an Agilent LC MSD SI (Parameters: Zorbax SB-C18 column, 1.8 μm, 4.6 mm, 15 mm, solvent acetonitrile–water (95:5), 0.1% trifluoroacetic acid, rate of elution 3ml/s; 1 μl sample injected; chemical ionization at atmospheric pressure with simultaneous scans of positive an negative ions with masse from 80-1000 *m/z*).

Institute of Organic Chemistry, Ukraine National Academy of Sciences, Kiev 02094; e-mail: Rostov@bcpi.kiev.ua. Translated from Khimiya Geterotsiklicheskikh Soedienii, No. 4, 618-619, April, 2007. Original article submitted November 17, 2006.

Compounds **3a,b** were prepared by method [1] and were dried in a vacuum of a water pump at 115°C for 5 h before elemental analysis.

1-Methyl-2-[1,5-diphenylpyrazol-4-yl)-1H-benzimidazole (3a). Yield 88%; mp 190-191.5°C. ^{1}H NMR spectrum, δ, ppm: 3.43 (3H, s, CH_3-1); 7.18-7.42 (12H, m, H-5,6 + CC_6H_5 + NC_6H_5); 7.47-7.50 (1H, m, H-7); 7.60-7.63 (1H, m, H-4); 8.10 (1H, s, H-3'). Chromatomass–spectrometric analysis: purity > 99%. Found: M + 1 = 351. Calculated: M = 350. Found, %: C 78.48; H 5.02; N 15.52. $C_{23}H_{18}N_4$. Calculated, %: C 78.83; H 5.18; N 15.99.

1-Methyl-2-[1-(4-nitrophenyl)-5-phenylpyrazol-4-yl]-1H-benzimidazole (3b). Yield 89%; mp 202-207.5°. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 3.46 (3H, s, CH_3-1); 7.19-7.43 (7H, H-5,6 + C_6H_5); 7.49-7.52 (1H, m, H-7); 7.57 and 7.28 (2 + 2H, two d, *J* = 9, $C_6H_4NO_2$); 7.61-7.64 (1H, m, H-4); 8.34 (1H, s, H-3'). Chromatomass–spectrometric analysis: Purity > 99%. Found: M+1 =396. Calculate: M = 395. Found, %: C 69.58; H 4.15; N 17.45. $C_{25}H_{18}N_4$. Calculated, %: C 69.86; H 4.33; N 17.71.

REFERENCES

1. I. B. Dzvinchuk and M. O. Lozinskii, *Khim. Geterotsikl. Soedin.,* 1404 (2005). [*Chem. Heterocycl. Comp.,* **41,** 1199 (2005)].
2. N. M. Elvan, *Tetrahedron,***60**, 1161 (2004).
3. V. G. Granik, A. M. Zhidkova, and R. G. Glushkov, *Uspekhi Khimii*, **46**, 685 (1977).
4. R. F. Abdulla and R. S. Brinkmeyer, *Tetrahedron*, **35**, 1675 (1979).
5. R. W. Middleton, H. Monney, and J. Parrick, *Synthesis*, 740 (1984).