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LETTERS TO THE EDITOR

RECYCLIZATION WITH DOUBLE HETEROCYCLIZATION ON FORMYLATION OF THE HYDRAZONE, 2-PHENACYL-1H-BENZIMIDAZOLE

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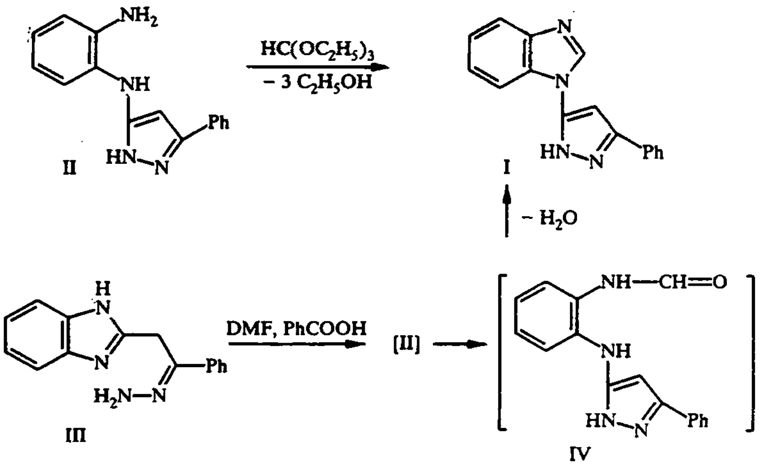
1-[3(5)-Phenylpyrazol-5(3)yl]-1H-benzimidazole (I) was obtained earlier in 50% yield by the reaction of 3(5)-[(*o*-aminophenyl)amino]-5(3)-phenylpyrazole (II) with ethyl orthoformate. We have developed a new method for its synthesis by boiling 2-phenacyl-1H-benzimidazole hydrazone with DMF in the presence of benzoic acid to give an 85% yield.



The reaction apparently occurs by ring opening of the benzimidazole ring and ring closing of the pyrazole ring to give the intermediate II. Further reaction with DMF gives the N-formyl derivative (IV), which undergoes intramolecular cyclocondensation under the reaction conditions with closing of a new benzimidazole ring. In the absence of benzoic acid, the reaction is unselective. It is very likely that the acid catalyzes the initial recyclization and also the subsequent formylation, being converted itself into N,N-dimethylbenzamide. Free dimethylamine was not observed in the reaction mixture.

We are developing the method by using more readily available starting materials, increasing the product yield and simplifying the synthetic procedure.

2-Phenacyl-1H-benzimidazole Hydrazone (III). 2-Phenacyl-1H-benzimidazole [2] (2.3 g, 10 mmol) and 30% aqueous hydrazine (3.0 cm^3, 30 mmol) in ethanol (5 cm^3) were boiled for 1 h. The produce precipitated on addition of water (3.5 cm^3) to the boiling solution. Yield 2.32 g (93%). M.p. 163.5-164.5°C (1-butanol). IR spectrum: 1635 (C=N), 3155, 3375 cm^{-1} (NH). ^{1}H NMR spectrum (DMSO-D$_6$): 4.22 (2 H, s, CH$_2$), 7.11-7.14 (2 H, m, 5-H and 6-H), 7.16 (2 H, br. s, NH$_2$), 7.21-7.35 (3 H, m, *p*- and 2*m*-H-Ph), 7.75-7.78 (2 H, m, 2*o*-H−Ph), 12.32 ppm (1 H, br. s, NH).

1,[3(5)-Phenylpyrazol-5(3)-yl]-1H-benzimidazole (I). Compound I (0.25 g, 1 mmol) and benzoic acid (0.13 g, 1.1 mmol) in DMF (1.0 cm^3) were boiled for 7 h. The product was precipitated by adding water (0.75 cm^3) to the boiling mixture.

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Yield 0.25 g (85%). M.p. 219-220.5°C (ethanol) lit.data [1]: 218-220°C; mixed melting point with a sample prepared according to [1], no depression. IR spectrum: 3025-3210 cm^{-1} (NH). ^1H NMR spectrum ($DMSO-D_6$): 7.20 (1 H, s, 4'-H), 7.25-7.40 (3 H, m, 4-H...6-H), 7.45-7.82 (5 H, m, Ph), 8.05 (1 H, d, J = 9 Hz, 7-H), 8.69 (1 H, s, 1-H), 13.50 ppm (1 H, br. s, NH). Data for 1-arylbenzimidazoles [3] were used for assigning the ^1H NMR spectrum.

Results of elemental analyses for compounds I and III agreed with calculated values.

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