The synthesis of condensed imidazoles I. A simple synthesis of some 1,5-diaryl-3-[2-(4,5-dimethyl-benzimidazol-2-yl)]formazans and their derivatives

Iveta Fryšová*, Jan Slouka, and Tomáš Gucký

Department of Organic Chemistry, Palacký University, Tř. Svobody 8, 771 46 Olomouc, Czech Republic
E-mail: frysova@orgchem.upol.cz
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Abstract
The condensation reaction of 1,5-diaryl-3-formazylglyoxylic acids (1) with 4,5-dimethyl-1,2-diaminobenzene affords 1,5-diaryl-3-[2-(4,5-dimethyl-benzimidazol-2-yl)]formazans (2) which have been transformed by reductive splitting into 5,6-dimethyl-benzimidazol-2-carboxamide arylhydrazones (3). Oxidative cyclization of formazanes (2) leads to the 2,3-diaryl-5-(4,5-dimethyl-benzimidazol-2-yl)tetrazolium chlorides (4). The corresponding picrates (5) also have been prepared.

Keywords: Formazylglyoxylic acid, 4,5-dimethyl-o-phenylenediamine, formazan

Introduction
The condensation reaction of α-ketocarboxylic acids with 1,2-diaminobenzene, which leads to 1,2-dihydroquinoxaline-2-ones, has been known for a long time.¹ It is a general method that proceeds high yields. A large number of substituted quinoxaline derivatives²⁻⁴ has been prepared in this way. We found that the course of reaction of 1,2-diaminobenzene with 1,5-diaryl-3-formazylglyoxylic acids proceeds in a different way; unexpectedly, 1,5-diaryl-3-(benzimidazol-2-yl)formazans are obtained instead of quinoxaline derivatives.⁵ Herein we focused on the preparation of a new group of 4,5-substituted-1,5-diaryl-3-[2-benzimidazol-2-yl]formazans (2), for which oxidative cyclization and reductive splitting were expected.

Results
A modification of Bamberger’s and Müller’s method⁶,⁷ was employed to prepare a series of 1,5-diaryl-3-formazylglyoxylic acids (1a-1f) by azocoupling of diazonium salts with sodium
pyruvate in alkaline medium. The condensation reaction of acids (1a-1f) with 4,5-dimethyl-1,2-diaminobenzene proceeded with simultaneous elimination of formic acid to afford 1,5-diaryl-3-[2-(4,5-dimethyl-benzimidazol-2-yl)]formazans (2a-2f). The oxidative cyclization of formazanes (2a-2f) was performed by the action of lead(IV) tetraacetate in chloroform, and the series of 2,3-diaryl-5-(2-oxo-1,2-dihydro-quinoxaline-3-yl)tetrazolium chlorides (4a-4f) was prepared. Compounds of the type 4 form their corresponding hydrates when crystallized from water. The chlorides were also transformed to the corresponding picrates (5a-5f). Reductive splitting of compounds (2a-2f) with H₂S proceeded smoothly to provide the corresponding benzimidazole-2-carboxamide arylhydrazones (3a-3f).

Experimental Section

1,5-Diaryl-3-[2-(4,5-dimethyl-benzimidazol-2-yl)]formazans 2a-2f. General procedure
The mixture of formazylglyoxylic acid (1a-1f) (1.00 mmol) and 4,5-dimethyl-1,2-diaminobenzene (136.2 mg; 1.00 mmol) refluxed for 5 min in ethanol (6.0 ml). After cooling to 20 °C, the red crystalline compound was filtered off, washed with water and dried. It was purified by recrystallization from ethanol. For further details see Tables 1-3 in the supplementary material section.

4,5-Dimethylbenzimidazole-2-carboxamidarylhydrazones 3a-3f. General procedure
A solution of corresponding 1,5-diaryl-3-[2-(4,5-dimethyl-benzimidazol-2-yl)]formazane (2a-2f) (1.00 mmol) in ethanol (50-150 ml) was saturated with H₂S. The solution was allowed to stand at room temperature in closed flask with intermittent stirring for 7 days. The reaction mixture was filtered and the filtrate was evaporated in vacuo. The solid was suspended in mixture of ethanol (5.0 ml) and water (3.0 ml) and allowed to stand at room temperature for 2 h. Then it was refluxed for 10 min and filtered hot. The filtrate was evaporated in vacuo. The product was crystallized from ethanol-water (1:1). For further details see Tables 1-3 in the supplementary material section.

2,3-Diaryl-5-(4,5-dimethyl-benzimidazol-2-yl)tetrazolium chlorides 4a-4f. General procedure
Lead(IV)tetraacetate (0.50 g; 1.12 mmol) was added with stirring to a solution of 1,5-diaryl-3-(4,5-dimethyl-benzimidazol-2-yl)formazan (2a-2f) (1.00 mmol) in CHCl₃ (50-150 ml). The solution was stirred for 3 h at room temperature and filtered. The filtrate was evaporated in vacuo, the residue dissolved in H₂O (10 ml) and acidified with conc. HCl to pH 2. The precipitate was filtered off and the filtrate was evaporated in vacuo. The residue was dissolved in methanol (7-10 ml), filtered and evaporated again. The residue was dried in vacuum dessicator over KOH. Compounds (4) are hygroscopic and they were transformed into less hygroscopic picrates. For further details see tables 1-3 in the supplementary material section.

2,3-Diaryl-5-(4,5-dimethyl-benzimidazol-2-yl)tetrazolium picrates 5a-5f. General procedure
A solution of sodium picrate (251.0 mg; 1.00 mmol) in H₂O (5 ml) was added to the stirred solution of tetrazolium salt (4a-4f) (1 mmol) in H₂O (1-3 ml) and stirring continued for 5
minutes. The precipitated compound (5a-5f) was collected with suction and dried. For further details see tables 1-3 in the supplementary material section.

Melting points (Boetius) are not corrected. Electronic spectra were recorded in ethanol solution on a UV-VIS spectrometer Unicam Helios α in 1 cm cuvettes. Concentrations of the samples varied from 0.5-1.10^{-5} mol.l^{-1}. Infrared spectra were recorded as potassium bromide disks and scanned on an ATI Unicam Genesis FTIR instrument. MS spectra were recorded on ZAB-EQ (VG Analytical Ltd., England). The NMR spectra were recorded in DMSO-d$_6$ solutions on a Bruker AMX-300 spectrometer (300MHz) with TMS as internal standard. Elemental analyses were performed using an EA Elemental Analyzer (Fison Instrument).

**Supplementary Material**

**Table 1.** Characteristic data of compounds 2-5.
**Table 2.** $^1$H-NMR spectra of compounds 2-3.
**Table 3.** IR spectra of compounds 2-3.

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**References**