

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, Tr. 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 method^{6,7} 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-(4,5-dimethyl-benzimidazol-2-yl)formazans 2a-2f. General procedure

The mixture of formazylglyoxylic acid⁶ (**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-carboxamidarylhyazones 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 dessiccator over KOH. Compounds (**4**) are hygroscopic and they were transformed into less hydroscopic 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-d₆ 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. ¹H-NMR spectra of compounds **2-3**.

Table 3. IR spectra of compounds **2-3**.

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