



Full paper/Mémoire

## Facile synthesis of trisubstituted imidazoles from 1,2-di(furan-2-yl)-2-oxoethyl carboxylates and their chemiluminescence

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### ARTICLE INFO

#### Article history:

Received 28 April 2012

Accepted after revision 13 June 2012

Available online 4 August 2012

#### Keywords:

Trisubstituted imidazoles

Microwave-assisted synthesis

1,2-di(furan-2-yl)-2-oxoethyl carboxylates

Solid support

Solvent-free

Chemiluminescence

### ABSTRACT

A facile synthesis of trisubstituted imidazoles containing furan rings was reported. Imidazoles were produced from 1,2-di(furan-2-yl)-2-oxoethyl carboxylates over solid alumina as solid support impregnated with ammonium acetate under solvent-free microwave-assisted conditions. The method possessed many remarkable advantages, such as the short reaction time (5–10 min), affording moderate to excellent yields and saving resources, conveniently operating process, which provided an attractive and environmentally-friendly approach for the synthesis of the important heterocyclic compounds. Moreover, the chemiluminescence property of some compounds synthesized has been investigated.

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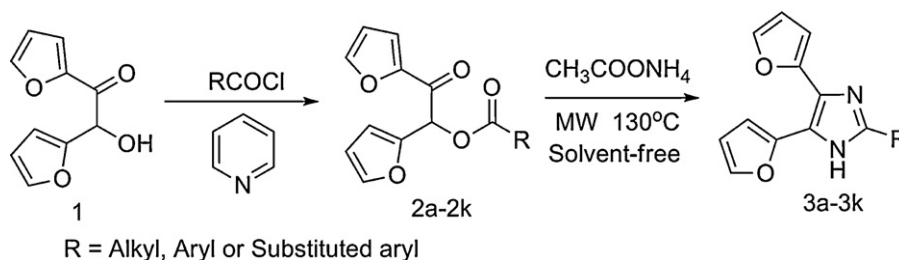
### 1. Introduction

Imidazole and its derivatives as a major kind of heterocyclic compounds play an important role in biochemistry [1–5], material chemistry including luminescent material [6,7] and proton conductivity material [8,9], medicinal chemistry [10–14] and the determination of heavy metal ion [15] and albumin in human serum samples [16] due to their structure nature. Therefore, effective methods for preparation of imidazole derivatives are of great interest in organic synthesis. The preparation for imidazole derivatives were usually based on the condensation of alkyl (aryl)-diones or 2-hydroxy-1,2-diphenylethanone with aldehydes, or  $\beta$ -carbonyl-N-acyl-N-alkylamines in the present of ammonium acetate, ammonia or primary amines in different solvent by various chemical methods like refluxing [17–20], solid-phase synthesis [21], heating in ionic liquid [22], sodium dihydrogen phosphate acted as catalyst [23], MW/silica-gel [24], MW/ $Al_2O_3$  [25], etc. However, many of the

methods reported above suffer from one or more disadvantages such as complex operation process, high solvent consumption and longer reaction time. Moreover, alkyl- or aryl-diones and aldehydes, benzoin and aldehydes were usually used as starting materials in these methods. Few methods were applied to the synthesis of furly-substituted imidazoles. Because the furan ring possess the inherent chemical properties and disadvantages, such as rich electron, lower conjugation energy, easily ring-opening in Brønsted acid, easily becoming yellow in oxygen and so on. Therefore, it is very significant to study and develop new scaleable synthetic routes able to construct fused imidazole derivatives in high yields. Especially imidazoles with furan rings which may extend the application of imidazole derivatives. For this purpose, microwave heating was introduced into the synthesis by allowing us to obtain rapid, reproducible, and scalable processes to synthesize new molecules in high yield. This methodology can facilitate the cyclization, and is well-suited for synthesizing the compounds with heterocyclic rings. In fact, traditional heating reactions often require high temperature for many hours or even days in the present of organic solvent, whereas similar or higher yields and cleaner process can be

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Scheme 1. The pathway of trisubstituted imidazoles containing furan rings.

obtained by microwave heating for a few minutes [13,24–28]. Our work focused on the synthesis of 2-substituted-4,5-di(2-furyl)imidazoles from 1,2-di(furan-2-yl)-2-oxoethyl carboxylates. It is known that the use of alumina or silica-gel in a solvent-free fashion greatly eases work-up procedures. To the best of our knowledge, the microwave-assisted and starting from 1,2-di(furan-2-yl)-2-oxoethyl carboxylates version of this reaction has not been reported, although several papers describing other microwave-assisted syntheses of imidazoles with benzene rings [24,25] and other synthesis of few furly-substituted imidazoles by heating in ionic liquid [22] have been published.

Herein, we wish to report a facile and environmentally-friendly method for the synthesis of trisubstituted imidazoles containing furan rings from 1,2-di(furan-2-yl)-2-oxoethyl carboxylates and using alumina as a safe, inexpensive solid support under solvent-free and microwave-assisted conditions (Scheme 1). In addition, when the method was used to synthesize trisubstituted imidazoles containing benzene rings, the desired products were also obtained. However, the yields were appreciably lower than that of trisubstituted imidazoles containing furan rings.

## 2. Experimental

Furoin (1,2-di(furan-2-yl)-2-hydroxyethanone) was generated from furfural according to the reported procedure [29]. All reagents were of analytical-reagent grade and used without further purification. All reported yields were isolated yields. All melting points were determined on a XT-4 melting point apparatus and were uncorrected.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were measured using a Varian Mercury-300 NMR spectrometer or a Bruker AVANCE-500 NMR spectrometer and with TMS as an internal standard. MS and HRMS were collected with an Agilent HP1100/6890 LC/MS spectrometer and an Agilent1290-micrOTOF Q II spectrometer, respectively. Elemental analyses were determined with a FlashEA1112 elemental analyzer. FT-IR spectra were obtained as KBr pellets using an IRAffinity-1 instrument in the range of 500–3500  $\text{cm}^{-1}$ . A MCL-3-type microwave reactor with a thermometer was used in all experiments (Microwave chemical lab, College of Electronics and Information Engineering, Sichuan University Sichuan, China). The CL emission was detected by an ultra-weak luminescence analyzer (type BPCL manufactured at the Institute of Biophysics, Chinese Academy of Sciences, Beijing, China). The acquisition and treatment of data were performed with BPCL software running under Windows XP.

### 2.1. Experimental procedures for compounds (2a–2k)

1,2-di(furan-2-yl)-2-oxoethyl carboxylates were synthesized according to the literature [30]. Furoin (5 mmol, 0.96 g) and acyl chlorides (5.5 mmol) were mixed in the three-neck flask. The mixture was heated to 30–40 °C in water bath with stirring for 15 min. Pyridine (3 mL) was slowly dropped into the mixture and stirred at the above temperature until the reaction was over by TLC analysis. Then the mixture was cooled, filtered and the residue was washed with iced ethanol (3 × 5 mL), water (3 × 10 mL), and recrystallized from 95% ethanol to give the pure product.

### 2.2. Experimental procedures for the synthesized compounds (3a–3k) under solvent-free condition

Typical procedure for the synthesis of trisubstituted imidazoles as follows: a mixture of alumina (0.8 g, 7.84 mmol) or silica-gel (0.5 g, 8.32 mol) ammonium acetate (0.23 g, 3 mmol) and 1,2-di(furan-2-yl)-2-oxoethyl carboxylates (1 mmol) was fully ground in a mortar, and then transferred to a 50 mL dried two-neck round-bottomed flask containing a thermometer and condenser, and heated with microwave irradiation for 5 min (the reaction temperature was 130 °C when the reaction was over.) or conventional heating at 130 °C for 40–90 min. The procedure was repeated twice. The reaction progress was monitored by TLC on Silufol-254 plates. When the microwave-assisted reaction was over, the residue was cooled to room temperature and was directly purified by column chromatography on Chemapol (200–300 mesh) silica gel (eluent, petroleum ether/ethyl acetate = 3/1) to give the desired products.

### 2.3. Physical and spectroscopic data

**4,5-di(furan-2-yl)-2-phenyl-1H-imidazole (3a)** Mp: 197–198 °C (lit. [21] 218 °C). Yield: 74.5%. IR (KBr):  $\nu$  ( $\text{cm}^{-1}$ ) 3118, 3054, 1599, 1551, 1481, 1404, 1233, 1090, 886, 732, 590.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm): 7.92 (dd,  $J=8.2, 1.5$  Hz, 2H), 7.57–7.33 (m, 5H), 6.99 (d,  $J=3.3$  Hz, 2H), 6.53 (dd,  $J=3.4, 1.8$  Hz, 2H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 146.74, 129.64, 129.52, 129.23, 125.96, 112.13, 108.00. MS,  $m/z$ : (M + H) $^+$  277.9, (M) $^+$  276.9 (Calcd 276.29). Anal. calcd for  $\text{C}_{17}\text{H}_{12}\text{N}_2\text{O}_2$ : C, 73.90; H, 4.38; N, 10.14. Found: C, 73.62; H, 4.34; N, 9.95.

**4,5-di(furan-2-yl)-2-(4-methylphenyl)-1H-imidazole (3b)** Mp: 217–219 °C. Yield: 75.5%. IR (KBr):  $\nu$  ( $\text{cm}^{-1}$ ) 3125,

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