Available online at www.sciencedirect.com

ScienceDirect

Chinese Chemical Letters 22 (2011) 793–796

CHINESE CHEMICAL LETTERS

www.elsevier.com/locate/cclet

Potassium ferro-cyanide trihydrate complex catalyzed one-pot synthesis of 2-phenylimidazo [4,5-*f*] [1,10] phenanthroline

Syed Shahed Ali *

Organic Laboratory, Department of Sir Sayyed College, Dr. Babasaheb Ambedkarb Marathwada University, Aurangabad 431001, India

Received 13 October 2010
Available online 17 April 2011

Abstract

Various 2-phenylimidazo [4,5-*f*] [1,10] phenanthrolines were synthesized from potassium ferro-cyanide trihydrate (KFCT) complex catalyzed three component reaction of 1,10-phenanthroline-5,6-dione, aromatic aldehydes and ammonium acetate at room temperature in excellent isolated yield. This is a simple and straight forward, high yielding, not involving any hazardous or expensive catalyst method.

© 2011 Syed Shahed Ali. Published by Elsevier B.V. on behalf of Chinese Chemical Society. All rights reserved.

Keywords: 2-Phenylimidazo [4,5-*f*] [1,10] phenanthrolines; Aromatic aldehyde; $K_4[Fe(CN)_6]\cdot 3H_2O$; Ammonium acetate

Imidazoles are heterocycles with a wide range of applications and are receiving growing attention [1]. The imidazole ring system is of particular interest because it is a component of histidine and its decarboxylation metabolite histamine [2]. The potency and wide applicability of the imidazole pharmacophore can be attributed to its hydrogen bond donor–acceptor capability as well as its high affinity for metals, which are present in many protein active site [3] (*e.g.* Zn, Fe, Mg). Also, improved pharmakinetics and bioavailability of peptide based protease inhibitors have been observed by replacing an amide bond with imidazoles [4]. In addition, the substituted imidazole ring systems are substantially used in ionic liquids [5] that have been given a new approach to "Green Chemistry". Due to their great importance, many synthetic strategies have been developed. In 1882, Radziszewki and Japp reported the first synthesis of the imidazoles from 1,2-dicarbonyl compound, various aldehydes and ammonia to obtain the imidazoles [6,7]. Also Siddiqui et al. proposed the synthesis of the imidazole using ionic liquids [8]. Recently, there are several methods reported in the literature for the synthesis of imidazoles using Zeolite HY/silica gel [9], $ZrCl_4$ [10], $NiCl_2\cdot 6H_2O$ [11], iodine [12], sodium bisulfate [13], acetic acid [14]. However these methods require prolonged reaction time and exotic reaction condition. Thus, the development of a new method for the synthesis of imidazoles derivatives would be highly desirable.

Multi-component condensations (MCCs) constitute an especially attractive synthesis strategy for rapid and efficient generation of molecules due to the fact that the products are formed in a single step and also the diversity could be achieved simply by varying the reacting components. The use of catalysts [15] potassium ferrocyanide trihydrate $K_4[Fe(CN)_6]\cdot 3H_2O$, hereafter KFCT, is a member of the family of crystals having the general formula $A_4[B(CN)_6]\cdot 3H_2O$ where A is K or NH_4 while B is Fe, Mn, Ru or Os. In crystalline KFCT the three water molecules

---

* Corresponding author.
E-mail address: Shahedali444@gmail.com.

1001-8417/$ – see front matter © 2011 Syed Shahed Ali. Published by Elsevier B.V. on behalf of Chinese Chemical Society. All rights reserved.
doi:10.1016/j.cclet.2011.01.017

are located in layers perpendicular to the (0 1 0) axis and between each layer there are two layers of the $Fe(CN)_6^{4-}$ groups interspersed by K^+ ions while the Fe^{2+} ion is located at the center of the regular octahedra formed by six cyanide ions [16]. This molecular-type ionic crystal undergoes an interesting second-order ferroelectric phase transition below room temperature, at 249 K. Herein, we were used potassium ferrocyanide trihydrate (KFCT) as a catalyst, it has gained a vast importance in organic synthesis due to their several advantages such as, operationally simplicity, no toxicity, reusability, low cost, and ease of isolation after completion of the reaction.

1. Experimental

All chemicals were purchased from Merck, Aldrich and Rankem Chemical Companies and used without further purification. The uncorrected melting points of compounds were taken in an open capillary in a paraffin bath. The progresses of the reactions were monitored by TLC (thin layer chromatography). IR spectra were recorded on Perkin-Elmer FT spectrophotometer in KBr disc. ^1H NMR spectra were recorded on an 300 MHz and 90 MHz FT-NMR spectrometer in $CDCl_3$ and DMSO as a solvent and chemical shift values are recorded in units δ relative to tetramethylsilane (Me_4Si) as an internal standard.

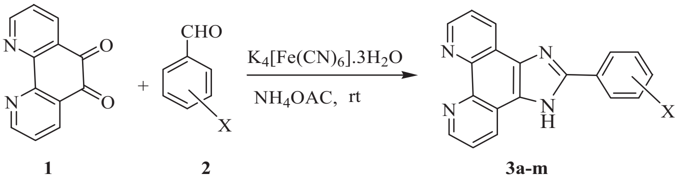
*1.1. General procedure for the synthesis of 2-phenylimidazo [4,5-f] [1,10] phenanthrolines **3(a-m)***

A mixture of aromatic aldehyde (1 mmol), 1,10-phenanthroline-5,6-dione (1 mmol), ammonium acetate (5 mmol), and $K_4[Fe(CN)_6]\cdot 3H_2O$ (15 mol%) were ground together in a mortar with a pestle at room temperature for appropriate time in (1 min). After completion of reaction confirmed by TLC, the mixture was treated with water to furnish the crude products. The crude was further purified by column chromatography by using petroleum ether:ethyl acetate (9:1) eluent and get the corresponding 2-phenylimidazo [4,5-*f*] [1,10] phenanthrolines **3(a-m)**. The products **3(a-m)** were confirmed by comparison with authentic sample, IR, ^1H NMR, mass, elemental analysis and melting points.

2. Results and discussion

As a part of our ongoing investigation in developing a versatile and efficient method for synthesis of heterocycles compounds [17–20] herein, we report efficient synthetic method for the synthesis of 2-phenylimidazo [4,5-*f*] [1,10] phenanthrolines from 1,10-phenanthroline-5,6-dione, substituted aromatic aldehyde and ammonium acetate in the presence of potassium ferrocyanide (Scheme 1).

Reaction was carried out simply by mixing 1,10-phenanthroline-5,6-dione with an aromatic aldehyde, ammonium acetate in the presence of a catalytic amount 15 mol% of $K_4[Fe(CN)_6]\cdot 3H_2O$ under solvent free condition. The mixture was ground to gather in a mortar with a pestle at room temperature for short reaction time, and then purified by column chromatography, substituted imidazole derivatives were obtained in excellent yields. Accordingly, (10 mol%) of catalyst was sufficient to catalyze the reaction. A rate enhancement with high yield was observed when higher molar ratios of $K_4[Fe(CN)_6]\cdot 3H_2O$ were used. However no product formation was observed in absence of $K_4[Fe(CN)_6]\cdot 3H_2O$. By getting this result, we have extended this protocol to a variety of aldehydes and ketones summarized in Table 1 This protocol is rapid and efficient for the preparation of several substituted imidazoles from both electrons efficient as well as electron deficient aromatic aldehydes. There is no effect on electron-withdrawing group and electron-donating group on reaction yield time. When aliphatic aldehyde and ketones (*e.g.* acetaldehyde, acetone) were also used as starting carbonyl compounds for the same reaction, no products formation took place in this reaction by grinding the reagents after extensive time more than 30 min. Different *ortho* and *para* phenyl group substituents did not show any effect on the formation rate of imidazoles. However, *meta* substitution requires



Scheme 1. Synthesis of 2-phenylimidazo [4,5-*f*] [1,10] phenanthroline **3(a-m)**.

Download English Version:

https://daneshyari.com/en/article/1255662

Download Persian Version:

https://daneshyari.com/article/1255662

Daneshyari.com