

Catalytic application of 1-(carboxymethyl)pyridinium iodide on the synthesis of pyranopyrazole derivatives



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ABSTRACT

In this investigation, acetic acid functionalized pyridinium salt, namely 1-(carboxymethyl)pyridinium iodide {[cmpy]I}, has been introduced as reusable catalyst for green, simple and efficient synthesis of 6-amino-4-(4-methoxyphenyl)-5-cyano-3-methyl-1-phenyl-1,4-dihydropyrano[2,3-c]pyrazoles by the one-pot tandem four-component condensation reaction of aryl aldehydes with ethyl acetoacetate, malononitrile and hydrazine hydrate at 100 °C under solvent-free conditions. Additionally, ¹H and ¹³C NMR, mass, CHN analysis, Fourier transform infrared spectroscopy (FT-IR), scanning electron microscope (SEM), thermal gravimetric analysis (TGA), differential thermal gravimetric (DTG), X-ray diffraction analysis (XRD), and calculation of crystallite size and inter planer distance of the catalyst have been investigated.

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1. Introduction

Tandem reaction, as a modern protocol in organic transformations, is a reaction in which several bonds are formed in some sequences without separating of any intermediates, changing reaction conditions and adding reagents. Clean reaction condition, high atomic economy and much complexity in one step are some important advantages of tandem reactions [1–5].

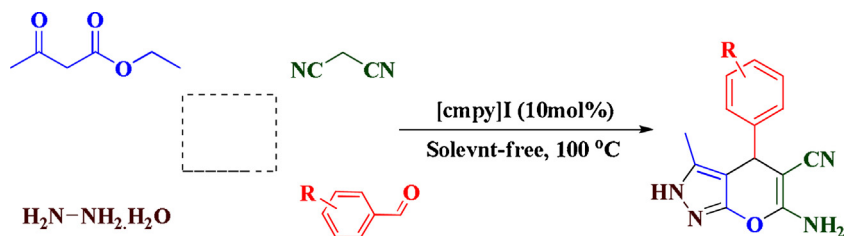
Pyranopyrazoles are interesting class of heterocyclic compounds; they have been used as fungicidal [6], bactericidal [7], vasodilatory [8] and anticancer [9]. They have also reported as pharmaceutical ingredients and biodegradable agrochemicals [10]. Additionally, pyrano[2,3-c]pyrazoles have been acted as potential insecticidal [11] and molluscicidal agents [12,13]. Several catalysts have been introduced for the synthesis of pyranopyrazoles, including imidazole [13], per-6-amino-b-cyclodextrin [14], phase transfer catalyst (HDBAC) [15], organocatalysts (MDOs) [16], D,L-Proline [17], hexa decyl tri methyl ammonium bromide (HTMAB) [18], disulfonic acid imidazolium chloroaluminate {[Dsim]AlCl₄} [19], gamma-alumina [20], magnetic Fe₃O₄ nanoparticles [21] and isonicotinic acid [22]. Therefore, considerable attention has been

focused on the development of new protocols for the preparation of these compounds.

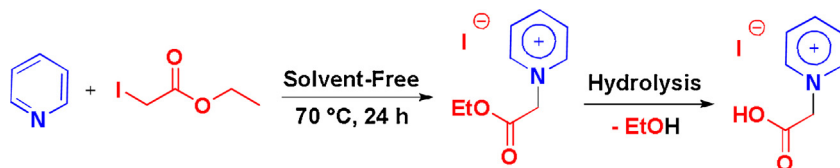
Recently, we have introduced a new category of ionic liquids and solid salts (with an organic cation), namely sulfonic acid functionalized imidazolium salts (SAFIS) [23–33]. In this class of salts, S–N bond formation in imidazole ring, as five member's heterocyclic compounds, was reported for the first time. These compounds have been successfully applied as catalysts or reagent for the synthesis of bis(indolyl) methanes [23], N-sulfonyl imines [24], 1-amidoalkyl-2-naphthols [25], various xanthene derivatives [26], 1-carbamatoalkyl-2-naphthols [27], 4,4'-(arylmethylene)-bis(3-methyl-1-phenyl-1H-pyrazol-5-ol)s [28], N-boc protected amines [29], hexahydroquinolines [30], nitroaromatic compounds [31,32], 1,2,4,5-tetrasubstituted imidazoles [33]. In continuation of our previous projects involving the preparation and applications of acidic ionic liquids and solid salts in organic transformations, we have used 1-(carboxymethyl) pyridinium iodide {[cmpy]I} on the synthesis of 6-amino-4-(4-methoxyphenyl)-5-cyano-3-methyl-1-phenyl-1,4-dihydropyrano[2,3-c]pyrazoles by the one-pot multi-component condensation reaction of arylaldehydes with ethyl acetoacetate, malononitrile and hydrazine hydrate (Scheme 1).

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Scheme 1. The preparation of pyranopyrazole derivatives using [cmpy].



Scheme 2. The synthesis of 1-(carboxymethyl) pyridinium iodide {[cmpy]}.

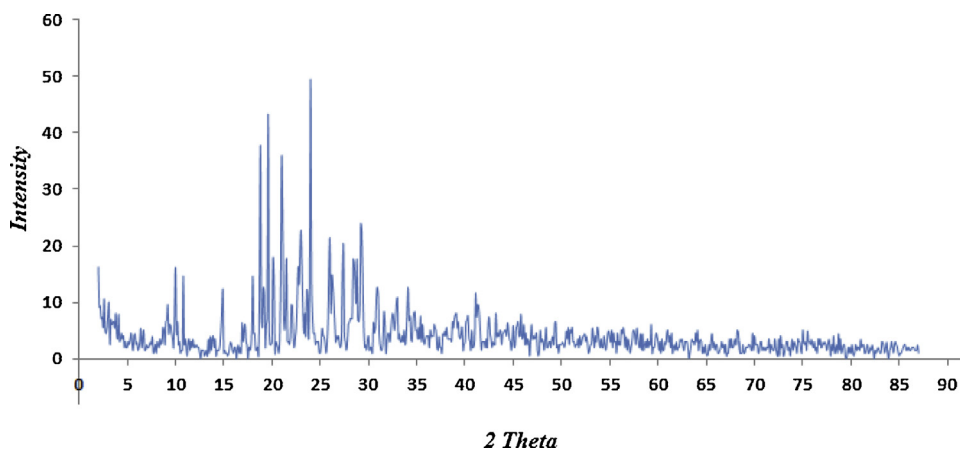


Fig. 1. The XRD pattern of 1-(carboxymethyl) pyridinium iodide [cmpy].

2. Experimental

2.1. General

All chemicals were purchased from Merck or Fluka Chemical Companies. The known products were identified by comparison of their melting points and spectral data with those reported in the literature. Progress of the reactions was monitored by TLC using silica gel SIL G/UV 254 plates. The ^1H NMR (400 MHz) and ^{13}C NMR (100 MHz) were recorded on a Bruker Avance DPX-250 FT-NMR spectrometer (δ in ppm). Infrared spectrum of products was recorded by PerkinElmer PE-1600-FTIR. Melting points were recorded on a Büchi B-545 apparatus in open capillary tubes.

2.2. Procedure for the synthesis of 1-(carboxymethyl) pyridinium iodide {[cmpy]}

A mixture of pyridine (0.010 mol) and ethyl iodoacetate (0.010 mol) was stirred and heated at 70 °C for 24 h. After this time, the reaction mixture turned to a dark viscous liquid. The liquid was washed with diethyl ether (3 \times 30 mL) and dried under vacuum for 2 h. Then, a solution of HCl 37% (0.011 mol) was added to prepare liquid and refluxed for 30 min. Finally, the solvent was removed under reduced pressure and the remaining solid was washed with diethyl ether to give the product as a yellowish powder.

2.3. General procedure for the synthesis of 6-amino-4-(4-methoxyphenyl)-5-cyano-3-methyl-1-phenyl-1,4-dihydropyrano[2,3-c]pyrazoles

A mixture of aromatic aldehyde (2 mmol), malononitrile (0.132 g, 2 mmol), ethyl acetoacetate (0.26 g, 2 mmol) hydrazine hydrate (2.5 mmol) and {[cmpy]}I (10 mol%) was added in a 10 mL round-bottomed flask connected to a reflux condenser, and stirred at 100 °C. After completion of the reaction, as monitored by TLC, H_2O (10 mL) was added to the reaction mixture, stirred and refluxed for 5 min. Then the reaction mixture was filtered and the solvent of the filtrate (H_2O) was removed under reduced pressure to separate the catalyst from crude product. The solid residue (crude product) was triturated by a mixture of ethanol and water (9/1) to obtain the pure product.

3. Results and discussion

1-(Carboxymethyl)pyridinium iodide {[cmpy]}I was synthesized by the reaction of pyridine with ethyl iodoacetate at 70 °C. Then, the product was hydrolysed to give [cmpy]. The structure of [cmpy]I was confirmed by ^1H NMR, ^{13}C NMR, IR and mass as well as CHN analysis (Scheme 2).

The IR spectrum of [cmpy]I has been shown in Fig. S1. The broad peak at 2493–3050 cm^{-1} can be related to O–H stretching of the COOH group. Also, the peak observed at 1734 cm^{-1} correspond to vibrational modes of C=O bond of the COOH group. Also, the C–H

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