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ORIGINAL ARTICLE

CuI-nanoparticles-catalyzed one-pot synthesis of benzo[*b*]furans via three-component coupling of aldehydes, amines and alkyne

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Abstract A novel application of copper iodide nanoparticles as an efficient catalyst has been developed for the synthesis of 2,3-disubstituted benzo[*b*]furan derivatives via three-component coupling of aldehydes, secondary amines and alkyne. The method presented is green, effective, inexpensive and satisfactory to give the products in high yields and short reaction times by the use of novel nanoscale materials.

1. Introduction

Nanotechnology has been one of the most attractive research areas in recent years. The reactivity and selectivity of nanoparticles as catalyst are largely determined by the energy of surface atoms, which can be easily gauged by the number of neighboring atoms by the bonding modes and accompanying energies of small molecules to be transformed on the nanoparticles surfaces (Min et al., 2008). Due to the non-additive nature of the catalytic properties of nanoparticles, research in the field of nanoparticles based catalysis has been focused on the preparation of small nanoparticles with high surface-to-volume ratios for high catalytic activity. The ability of nanotechnology to enhance catalytic activity opens the potential to replace expensive catalysts with lower amounts of inexpensive nanocatalysts (Bing et al., 2007).

Among various metal nanoparticles, copper nanoparticles have received much attention because of their unusual properties and potential applications in diverse fields (Lu et al., 2000). Copper nanoparticles have been used as a low-priced catalyst in industry and catalysis of many organic transformations (Kantam et al., 2006). Recently, copper nanoparticles were used as an active catalyst in many reactions including carbon–heteroatom coupling (Rout et al., 2007; Suribabu et al., 2009), synthesis of phenols, anilines, and thiophenols (Hua-Jian et al., 2011), alkyne-azide cycloadditions (Song et al., 2008), the Mannich reaction (Kidwai et al., 2009), aza-Michael reactions (Beck et al., 1995) and hydroxylation of phenol (Edward et al., 2010).

The research in multi-component reactions (MCRs) is an encouraging and hot topic of organic chemistry because of their advantages in the preparation of small molecule libraries and in drug discovery procedures (Thompson and Ellman, 1996). Also MCRs are efficient, environmentally friendly, fast, atom economic and time-saving. They supply an effective tool

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for the preparation of various compounds with pharmaceutical and biological properties (Negwar, 1994).

Three-component reaction of aldehydes, amines and alkynes (A^3 coupling) has received much attention in recent years. Some biologically active heterocyclic compounds such as propargylamines, imidazo[1,2*a*] pyridines and benzofurans (Black and Arndtsen, 2004) are the result of A^3 coupling reactions. The benzo[*b*]furans are important heterocyclic compounds, which not only act as key structural subunits in naturally occurring compounds that exhibit remarkable biological activities but also represent useful building blocks in the synthesis of natural products (Simpson and Thomson, 1985; Bird and Cheeseman, 1984).

Derivatives of these compounds are known to possess important pharmaceutical (Buu-Hoi et al., 1957), antifungal (Benkli et al., 2003), antitumor (Baraldi et al., 2000) and other bioorganic properties (Li et al., 2005). In addition, benzofurans are used in cosmetic formulations (Leung and Foster, 1996) and have application as synthetic precursors for optical brighteners (Elvers et al., 1999).

Designing of new methods for the preparation of benzofurans has always been considered. The synthetic ways for the preparation of benzo[*b*]furans mainly are dehydrative annulation of phenols bearing appropriate ortho vinyllic substituents (Thielges et al., 2004), intramolecular cyclization of substituted allyl–aryl ethers(Hennings et al., 1997), [3,3]-sigmatropic rearrangement of various arenes (Sheradsky, 1966), dehydrative cyclization of α-(phenoxy)-alkyl ketones (Wright, 1960), Sonogashira cross-coupling reaction of 2-iodonitrophenol acetates (Dai and Lai, 2002), coupling of *o*-iodophenols and aryl acetylenes (Astruc, 2007) and the cyclization reaction of 2-hydroxybenzaldehydes, amines and alkynes using various catalysts (Hongfeng et al., 2009; Sakai et al., 2008).

The organic reactions in aqueous media have attracted much attention in synthetic organic chemistry, because water is one of the most abundant, cheapest and environmentally friendly solvents and it also exhibits unique reactivity and selectivity in comparison with conventional organic solvents (Li and Chan, 1997). The significant enhancement in the rate of the reaction has been attributed to hydrophobic packing, solvent polarity, hydration and hydrogen bonding of water (Rideout and Breslow, 1980). Thus, the use of water instead of organic solvents is an essential component of sustainable chemistry (Yadav et al., 2007).

In accord to the significance of carbon–carbon and carbon–heteroatom bond formation and also in continuation of our research on the application of nanocatalysts in organic synthesis (Safaei-Ghomi and Ghasemzadeh, 2012; Safaei-Ghomi et al., 2012), herein we have explored the A^3 coupling of aldehydes, amines and alkynes in the presence of CuI nanoparticles for the synthesis of benzofuran derivatives (Scheme 1).

2. Experimental

2.1. Materials and methods

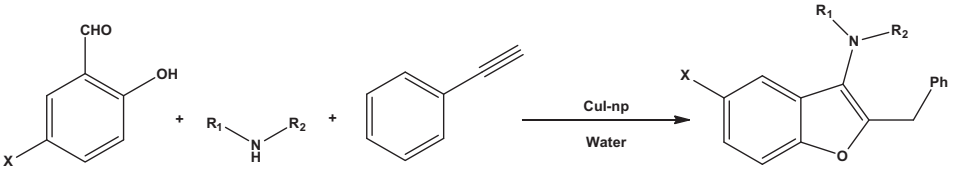
Chemicals were purchased from the Sigma–Aldrich and Merck in high purity. All the materials were of commercial reagent grade and were used without further purification. Copper iodide nanoparticles were prepared according to the procedure reported by Yang et al. (2005). Flash-column chromatography was performed by using Merck silica gel 60 with freshly distilled solvents. All melting points are uncorrected and were determined in capillary tube on Boetius melting point microscope. ^{1}H NMR and ^{13}C NMR spectra were obtained on Bruker 400 MHZ spectrometer with $CDCl_3$ as solvent using tetramethylsilane (TMS) as an internal standard, the chemical shift values are in δ. FT-IR spectrum was recorded on Magna-IR, spectrometer 550 Nicolet in KBr pellets in the range of 400–4000 cm^{-1}. The elemental analyses (C, H, N) were obtained from a Carlo ERBA Model EA 1108 analyzer. The N_2 adsorption/desorption analysis (BET) was performed at −196 °C using an automated gas adsorption analyzer (Tristar 3000, Micromeritics). Powder X-ray diffraction (XRD) was carried out on a Philips diffractometer of X'pert Company with mono chromatized Cu Kα radiation (λ = 1.5406 Å). The compositional analysis was done by energy dispersive analysis of X-ray (EDAX, Kevex, Delta Class I). Microscopic morphology of products was visualized by SEM (LEO 1455VP). The mass spectra were recorded on a Joel D-30 instrument at an ionization potential of 70 eV.

2.2. Preparation of CuI nanoparticles

The mixture of copper iodide (0.1 g, 0.5 mmol) in 5 mL of acetonitrile was dissolved under ultrasonic irradiation. Afterward DMF (10 mL) was added to the solution and the mixture was sonicated to afford a yellowish solution. The reaction mixture was heated at 25 °C to remove acetonitrile and then 10 mL of water was added dropwise to the solution under mechanical stirring. The cloudy green precipitate residue was centrifuged and also washed several times with ethanol to afford pure CuI nanoparticles. The prepared nanoparticles were fully characterized by SEM, XRD and EDAX analyses.

2.3. General procedure for the synthesis of 2,3-disubstituted benzofurans (*4a–l*)

To a stirring solution of salicylaldehyde (2 mmol), secondary amine (1 mmol) and phenyl acetylene (1.5 mmol) in 5 ml of water, was added CuI NPs (0.1 mmol) and K_2CO_3 (1.0 mmol) at room temperature. Then the resulting mixture was refluxed



Scheme 1 Three-component coupling of salicylaldehydes, amines and phenylacetylene catalyzed by copper iodide nanoparticles in water.