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Effective preparation of 2-amino-3-cyano-4-aryl-5,10-dioxo-5,10-dihydro-4*H*-benzo[g]chromene and hydroxyl naphthalene-1,4-dione derivatives under ambient and solvent-free conditions

Hamid Reza Shaterian *, Majid Mohammadnia

Department of Chemistry, Faculty of Sciences, University of Sistan and Baluchestan, PO Box 98135-674, Zahedan, Iran

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ABSTRACT

The mild basic ionic liquids, 1,8-diazabicyclo[5.4.0]-undec-7-en-8-ium acetate, pyrrolidinium acetate, pyrrolidinium formate, piperidinium acetate, piperidinium formate, *N*-methylimidazolium formate, and 3-hydroxypropanaminium acetate catalyzed three-component synthesis of 2-amino-3-cyano-4-aryl-5,10-dioxo-5,10-dihydro-4*H*-benzo[g]chromene and hydroxyl naphthalene-1,4-dione derivatives under ambient and solvent-free conditions. Simple procedure, high yields, short reaction time and environmentally benign method are advantages of these protocols. The inexpensive and non-toxic ionic liquids can be reused several times without noticeable loss of their activities. The mentioned ionic liquids show priority relative to other catalysts in the literature.

1. Introduction

Due to their unique properties, ionic liquids (ILs) have become increasingly popular over the last few years in the field of green organic synthesis [1]. ILs can be used as reaction media and catalyst for organic syntheses [2]. The greener Ils show several advantages including their easy work-up by straightforward extraction, high-yield isolation and purification, homogenous and mild reaction conditions, and efficient reusability [3]. The functionalized ionic liquids are used instead of classical volatile organic compounds in organic reactions [4]. In a literature review, researchers collect information about this topic [1–5] and use ILs as environmental friendly solvents and catalysts in the green organic chemistry field.

Multi-component reactions (MCRs) have proven to be a valuable asset in organic and medicinal chemistry; such protocols can be used for drug design, and drug discovery because of their simplicity, efficiency, and high selectivity [6,7]. Synthesis of bioactive and complex molecules should be facile, fast, and efficient with minimal workup in this methodology [6–8].

In continuation of our research on ionic liquids and their applications as catalyst in green organic synthesis [9–11], herein, we reported an efficient method for three component synthesis of 2-amino-3-cyano-4-aryl-5,10-dioxo-5,10-dihydro-4*H*-benzo[g]chromene derivatives using weak basic ionic liquids such as 1,8-diazabicyclo[5.4.0]-undec-7-en-8-ium acetate (DBU[CH_3COO]), pyrrolidinium acetate ([Pyrr][CH_3COO]), pyrrolidinium formate ([Pyrr][HCOO]), piperidinium acetate ([Pip][CH_3COO]), piperidinium formate ([Pip][HCOO]), *N*-methylimidazolium formate ([Hmim][HCOO]), and 3-hydroxypropanaminium acetate (3-HPAA) as catalysts for condensation reaction of aromatic aldehydes, malononitrile, and 2-hydroxynaphthalene-1,4-dione under ambient and solvent-free conditions for the first time (Scheme 1).

We also used these environmental friendly ionic liquids in condensation reaction of aromatic aldehydes, aromatic amines, and 2-hydroxynaphthalene-1,4-dione for preparation of hydroxyl naphthalene-1,4-dione derivatives under ambient and solvent-free conditions (Scheme 2).

Literature survey showed us that few research studies were done on DBU[CH_3COO], [Pyrr][CH_3COO], [Pyrr][HCOO], [Pip][CH_3COO], [Pip][HCOO], [Hmim][HCOO], and 3-HPAA. DBU[CH_3COO] was used in aza-conjugate addition of amines to various electron deficient alkenes [12]. [Pyrr][CH_3COO] was applied in Knoevenagel condensation [13]. Synthesis and characterization of [Pyrr][HCOO] [14] and its transport properties [15] were investigated. Piperidinium acetate was found to be a tandem catalyst in Knoevenagel condensation, Nazarov cyclization, and Conia-ene reactions [16]; this catalyst also was used in synthesis of ethyl 6-substituted-2-hydroxy-2-(trifluoromethyl)-2*H*-chromene-3-carboxylates [17]. Electrochemical and physicochemical properties of [Pip][HCOO] [18] were studied. "Living" radical polymerization of methyl methacrylate [19] and also the atom transfer radical polymerization (ATRP) of methyl methacrylate (MMA) employing

* Corresponding author. Tel.: +98 541 2446565; fax: +98 541 2431067.
E-mail address: hrshaterian@chem.usb.ac.ir (H.R. Shaterian).

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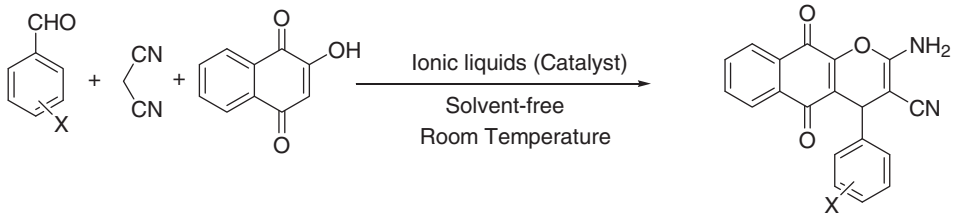


Ionic Liquids = 1,8-diazabicyclo[5.4.0]-undec-7-en-8-ium acetate (DBU[CH_3COO]), pyrrolidinium acetate ([Pyrr][CH_3COO]), pyrrolidinium formate ([Pyrr][HCOO]), piperidinium acetate ([Pip][CH_3COO]), piperidinium formate ([Pip][HCOO]), N-methylimidazolium formate ([Hmim][HCOO]), and 3-hydroxypropanaminium acetate (3-HPAA)

Scheme 1. Synthesis of 2-amino-3-cyano-4-aryl-5,10-dioxo-5,10-dihydro-4*H*-benzo[g]chromene derivatives.

ethyl 2-bromoisobutyrate (EBiB)/CuBr as the initiating system using *N*-methylimidazolium formate ([Hmim][HCOO]) were reported [20]. 3-HPAA as a new weak basic ionic liquid was used in the preparation of 2-amino-5-oxo-4,5-dihydropyrano[3,2-c]chromene-3-carbonitrile derivatives [11].

2-Amino-3-cyano-4-aryl-5,10-dioxo-5,10-dihydro-4*H*-benzo[g] chromene derivatives show a variety of biological activities, including anticancer [21], anti-inflammatory [22], antimalarial [23,24], and pesticide activities [25]. Hydroxyl naphthalene-1,4-dione derivatives are fluorescent heterocyclic compounds. These fluorescent materials are of interest in many disciplines such as emitters for electroluminescence devices [26], molecular probes for biochemical research [27], in traditional textile and polymer fields [28], and fluorescent whitening agents [29].

2. Experimental

All reagents were purchased from Merck and Aldrich and used without further purification. The weak basic ionic liquids such as DBU[CH_3COO] [12], [Pyrr][CH_3COO] [13], [Pyrr][HCOO] [14], [Pip][CH_3COO] [16], [Pip][HCOO] [18], [Hmim][HCOO] [20], and 3-HPAA [11] were prepared according to the reported procedure. All yields refer to isolated products after purification. The NMR spectra were recorded on a Bruker Avance DPX 300 MHz instrument. The spectra were measured in DMSO-d_6 relative to TMS (0.00 ppm). IR spectra were recorded on a JASCO FT-IR 460 plus spectrophotometer. Melting points were determined in open capillaries with a BUCHI 510 melting point apparatus. TLC was performed on silica-gel Poly Gram SIL G/UV 254 plates.

2.1. General procedure for the synthesis of 2-amino-3-cyano-4-aryl-5, 10-dioxo-5,10-dihydro-4H-benzo[g]chromene under solvent-free and ambient conditions

The mixture of the aldehydes (10 mmol), malononitrile (10 mmol), 2-hydroxynaphthalene-1,4-dione (10 mmol) and ionic liquids containing DBU[CH_3COO] (10 mol%), [Pyrr][CH_3COO] (15 mol%), [Pyrr][HCOO] (15 mol%), [Pip][CH_3COO] (10 mol%), [Pip][HCOO] (10 mol%), [Hmim][HCOO] (15 mol%), and 3-HPAA (15 mol%) as weak basic catalyst was stirred under ambient and solvent-free conditions for the specific time. After completion of the reaction, 5 mL of water was added to the mixture. The ionic liquid was dissolved in water and filtered for separation of the crude product. The separated product was washed twice with water (2×5 mL). The solid product was purified by recrystallization procedure in ethanol. All of the desired product(s) were characterized by comparison of their physical data with those of known compounds. For recycling the catalysts, after washing solid products with water completely, the water containing ionic liquid (IL is soluble in water) was evaporated under reduced pressure and ionic liquid was recovered and reused.

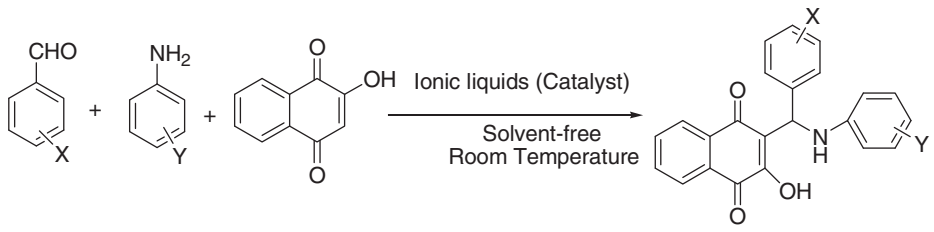
Selected spectra for two known products are given below:

2-Amino-3-cyano-4-(2,4-dichlorophenyl)-5,10-dioxo-5,10-dihydro-4*H*-benzo[g]chromene (Table 2, Entry 13): orange powder; mp = 288 °C; IR (KBr): ν_{max} = 3467, 3341, 3168, 2201, 1664, 1631, 1591, 1364, 1247, and 1200 cm^{-1}.; ^1H NMR (300 MHz, DMSO-d_6): δ = 4.74 (^1H, s, CH), 8.08–7.48 (9 H, m, Ar) and NH_2) ppm.; ^{13}C NMR(75 MHz, DMSO-d_6): δ = 37.1, 56.9, 110.3, 119.2, 119.5, 121.1, 126.2 (2C), 126.5, 129.3, 131.2, 131.3, 133.1, 136.6 (2C), 136.9, 149.5, 158.1, 177.2, and 183.6 ppm.

2-Amino-3-cyano-4-(2-nitrophenyl)-5,10-dioxo-5,10-dihydro-4-*H*-benzo[g]chromene (Table 2, Entry 15): orange powder; mp = >243 °C; IR (KBr): ν_{max} = 3429, 3338, 2207, 1666, and 1631 cm^{-1}.; ^1H NMR (300 MHz, DMSO-d_6): δ = 5.94 (^1H, s, CH), 8.27–7.46 (10 H, m, Ar and NH_2) ppm.; ^{13}C NMR(75 MHz, DMSO-d_6): δ = 31.5, 55.2, 119.2, 121.6, 124.5, 126.3, 127.0, 128.9, 131.0, 131.2, 131.8, 134.3, 134.7, 135.1, 138.3, 149.0, 149.5, 159.4, 177.2, and 183.2 ppm.

2.2. Synthesis of hydroxyl naphthalene-1,4-dione derivatives under ambient and solvent-free conditions

The mixture of the aldehydes (10 mmol), anilines (10 mmol), 2-hydroxynaphthalene-1,4-dione (10 mmol) and ionic liquids containing



Ionic Liquids = 1,8-diazabicyclo[5.4.0]-undec-7-en-8-ium acetate (DBU[CH_3COO]), pyrrolidinium acetate ([Pyrr][CH_3COO]), pyrrolidinium formate ([Pyrr][HCOO]), piperidinium acetate ([Pip][CH_3COO]), piperidinium formate ([Pip][HCOO]), N-methylimidazolium formate ([Hmim][HCOO]),and 3-hydroxypropanaminium acetate (3-HPAA)

Scheme 2. Synthesis of hydroxyl naphthalene-1,4-dione derivatives.