Journal of Saudi Chemical Society (2015) 19, 628–633

King Saud University

Journal of Saudi Chemical Society

www.ksu.edu.sa
www.sciencedirect.com

ORIGINAL ARTICLE

An investigation of the catalytic potential of potassium cyanide and imidazolium salts for ultrasound-assisted synthesis of benzoin derivatives

Javad Safari [a,*], Zohre Zarnegar [a], Masoume Ahmadi [a], Susan Seyyedi [b]

[a] *Laboratory of Organic Compound Research, Department of Organic Chemistry, College of Chemistry, University of Kashan, P.O. Box 87317-51167, Kashan, I.R., Iran*
[b] *Faculty of Science, DareShahr Branch, Islamic Azad University, Ilam, I.R., Iran*

Received 25 March 2012; accepted 18 May 2012
Available online 29 May 2012

KEYWORDS

Benzoin condensation;
Catalysts;
Cyanide ion;
Imidazolium salts;
Ultrasonic

Abstract A rapid, highly efficient and mild green synthesis of benzoin was performed using substituted benzaldehyde catalyzed by KCN and imidazolium salts in EtOH/H_2O under ultrasonic activation. The products were obtained in good yields within short reaction times with *N*,*N*′-dialkylimidazolium salts, which were found to be more effective pre-catalysts at room temperature for benzoin condensation in comparison to corresponding cyanide ion in heating method. This simple method affords benzoin derivatives at room temperature in short reaction times with high yield and purity.

© 2012 Production and hosting by Elsevier B.V. on behalf of King Saud University.

1. Introduction

The formation of carbon–carbon bond is one of the most fundamental reaction for the construction of a molecular framework (Trost, 1991; Basavaiah et al., 2003). In past decades, several carbon–carbon bond-forming reactions have been discovered and their applications in organic chemistry have also been well documented in the literature (Sammelson and Kurth, 2003; Huddleston and Krische, 2003; Gibson and Stevenazzi, 2003; Moreno-Mañas and Pleixats, 2003). Among these reactions, the benzoin condensation is an important method for the formation of carbon–carbon bonds starting from aldehydes giving α-hydroxycarbonyl compounds, which are interesting building blocks for the synthesis of natural and pharmaceutical compounds (Iwamato et al., 2006; Konosu et al., 1991).

After the first report by Wöhler and Liebig who used cyanide as a pre-catalyst in 1832 (Wöhler and Liebig, 1832), various catalysts have been used to promote the benzoin condensation reaction effectively. Breslow in 1958 first recognized that the N-heterocyclic carbenes (NHCs) could also serve all these roles similar to that of cyanide ion in benzoin condensation (Breslow, 1958), and NHCs are better nucleophiles and leaving groups than cyanide. Nevertheless, the discovery of stable carbenes by Arduengo in 1991 (Arduengo et al., 1991) provided the access to develop a variety of NHC catalysts for benzoin condensation (Mavis et al., 2010; Baragwanath et al., 2009; Toole et al., 2011).

* Corresponding author. Tel.: +98 361 5912894; fax: +98 361 5912320.
E-mail address: safari@kashanu.ac.ir (J. Safari).
Peer review under responsibility of King Saud University.

ELSEVIER Production and hosting by Elsevier

1319-6103 © 2012 Production and hosting by Elsevier B.V. on behalf of King Saud University.
http://dx.doi.org/10.1016/j.jscs.2012.05.005

The use of NHCs such as thiazolium (Knight and Leeper, 1998), triazolium (Enders and Han, 2008), imidazolium (Orsini et al., 2009) and benzimidazolium (Pesch et al., 2004) salts has resulted in steady improvements of the yields and selectivities. Different reaction conditions have been studied to obtain milder and simpler methods for the benzoin condensation (Storey and Williamson, 2005; Xu et al., 2005). A number of recent reports however, have described efficient imidazole based carbene catalysts with the advantage of trivial catalyst synthesis, and increased stability over other heterocyclic systems (Orlandi et al., 2003). There still appears a need to introduce novel methods to permit better selectivity under milder conditions and with easy work-up procedures. Ultrasonic irradiation has been considered as a clean and useful protocol in organic synthesis during the last three decades, compared with traditional methods, the procedure is more convenient. A large number of organic reactions can be carried out in higher yield, shorter reaction time or milder conditions under ultrasonic irradiation (Safari and Moshtael Arani, 2011; Safari et al., 2010; Estager et al., 2007).

Herein, we wish to report the synthesis of symmetrical and unsymmetrical benzoin derivatives using potassium cyanide and imidazolium salts in ethanol–water binary mixtures under ultrasound (Scheme 1).

We found that the imidazolium salts efficiently catalyze the benzoin condensation of aldehydes in the presence of a base. Hence, our interest focused on an investigation of the effect of tricationic and dicationic NHCs in this reaction under ultrasound. These tricationic and dicationic imidazolium salts show considerable catalytic potential when compared with monocationic imidazolium salts and toxic cyanide anions. This paper describes for the first time, the use of tricationic imidazolium salts in the acyloin condensation under ultrasound. This simple method affords benzoin derivatives at room temperature in short reaction times with high yield and purity.

2. Experimental

2.1. Materials and instruments

In a typical procedure, chemicals were purchased from Merck chemical company. The *N*,*N*′-dialkyl imidazolium salts were prepared using the published procedure (Estager et al., 2002; Bonhôte et al., 1996; Tulloch et al., 2000). ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on a Bruker DPX-400 Avance spectrometer. Tetramethyl silane (TMS) was used as an internal reference. IR spectra were obtained on a Magna-550 Nicolet instrument. Vibrational transition frequencies were reported as wave numbers (cm^{-1}), and band intensities designated as weak (w), medium (m) and strong (s). A mass spectrum was recorded by a QP-1100EX Shimadzu spectrometer. Sonication was performed in a UP 400S ultrasonic processor equipped with a 3 mm wide and 140 mm long probe, which was immersed directly into the reaction mixture. The operating frequency was 30 kHz and the output power was 0–400 W through manual adjustment. UV spectra were recorded on a Hitachi 200–20 spectrometer using spectrophotometric grade ethanol (Baker). Melting points were obtained with a micro melting point apparatus (Electrothermal, Mk3) and are uncorrected.

2.2. General procedure for synthesis of *a*–*m*

2.2.1. KCN-catalyzed benzoin condensation under ultrasound irradiation

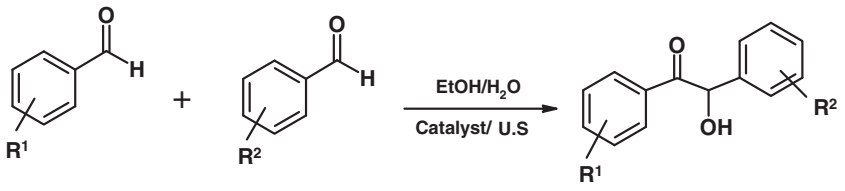
*General procedure for synthesis of **a**–**h**:* To synthesize the symmetrical benzoins, a solution of 1 mmol of benzaldehyde and 1 mmol of potassium cyanide (96–98 %) is mixed in water–ethanol mixtures (water:ethanol, 1:5 v/v). This reaction was completed under ultrasound irradiation at 80 °C for the appropriate amount of time to complete the reaction. The completion of reaction was monitored by TLC (petroleum ether:ethyl acetate, 4:1 v/v). The reaction mixture was cooled and the product was collected by vacuum filtration and washed thoroughly with water. The product was recrystallized from ethanol.

*General procedure for synthesis of **i**–**m**:* To synthesize the unsymmetrical benzoins, 1 mmol of donor benzaldehyde, 1 mmol of acceptor benzaldehyde, and 1 mmol of potassium cyanide are mixed in water–ethanol mixtures (water:ethanol, 1:5 v/v). This reaction was completed under ultrasound irradiation at 80 °C. The completion of reaction was monitored by TLC (petroleum ether:ethyl acetate, 4:1 v/v). The reaction mixture was cooled and the product was collected by vacuum filtration and washed thoroughly with water. The product was recrystallized from ethanol.

2.2.2. Imidazolium salts-catalyzed benzoin condensation under ultrasound irradiation

Three *N*,*N*′-dialkylimidazolium salts, [EtMeIm]Br, $[C_6H_4(CH_2ImMe)_2]Br_2$ and $[C_6Me_3(CH_2ImMe)_3]Br_3$ were prepared according to reported procedures in the literature (Iwamato et al., 2006; Kankala et al., 2011; Knight and Leeper, 1998; Sammelson and Kurth, 2001) (Scheme 2).

*General procedure for synthesis of **a**–**h**:* To a solution of the 1 mmol aldehyde in water–ethanol mixtures (water:ethanol, 1:5 v/v), 1 mol % catalyst and 20 mol % NaOH in 3 mL of H_2O were added, and the mixture was exposed to ultrasonic irradiation at room temperature for the appropriate amount of time to complete the reaction, The completion of reaction was monitored by TLC (petroleum ether:ethyl acetate, 4:1 v/v). The reaction mixture was cooled and the product was



Scheme 1 Preparation of benzoin with cyanide and imidazolium salts under ultrasound irradiation.

Download English Version:

https://daneshyari.com/en/article/229538

Download Persian Version:

https://daneshyari.com/article/229538

Daneshyari.com