IRANIAN JOURNAL OF CATALYSIS

Citric acid as an efficient and green catalyst for the synthesis of hexabenzyl hexaazaisowurtzitane (HBIW)

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Received 16 June 2015; received in revised form 5 August 2015; accepted 16 August 2015

ABSTRACT

The condensation of benzylamine with glyoxal leads to Hexabenzylhexaazaisowurtzitane (HBIW) in acetonitrile solvent with citric acid as a green catalyst under both conventional stirring and ultrasonic irradiation conditions. The influence of four variables, including the amount of catalyst, solvent, reaction time and ultrasonic power, on the reaction yield was investigated. The results showed that the optimum parameters for synthesis of HBIW were 5% mol with respect to glyoxal for catalyst, acetonitrile-water as solvent, 5 minutes as reaction time and 150 W for ultrasonic power. In general, improvement in rates and yields were observed when the reactions were carried out under sonication in comparison with classic conditions.

Keywords: *Hexabenzylhexaazaisowurtzitane (HBIW), Citric acid, Green chemistry, Ultrasound irradiation.*

1. Introduction

The purpose of Green Chemistry (GC) is the design of chemical products and making processes to decrease their impact on human health and environment. Essential to the GC concept is the idea of sustainability–reducing environmental impacts and conserving natural resources for future descendant [1,2]. In the past two decades, special attention has been paying to green chemistry. Green chemistry in the early 1990s, the scientific community has adopted a new approach to chemistry [3]. Catalysts play a significant role in green chemistry by performing different useful tasks [4-7]. They reduce energy requirements, increase selectivity, and permit the use of less dangerous reaction conditions. Citric acid as catalytic is green and efficient in organic chemistry [8,9].

Citric acid (2-hydroxy propane-1,2,3-tricarboxylic acid) was first isolated and crystallized from lemon juice by Karl Wilhelm Scheele in 1784 [10]. In 1937, Krebs discovered that citric acid is a central compound in aerobic metabolism through the tricarboxylic acid (TCA) cycle [11]. This organic acid is found as a natural constituent of a variety of citrus fruits, lemon, orange, pineapple, pear, peach, and fig [12,13]. The widespread presence of citric acid in the plant and animal is an assurance of its nontoxic nature, and nowadays citric acid is accepted as generally recognized as safe (GRAS) by the Joint FAO/WHO Expert Committee on Food Additives. Citric acid has been also used as a complexing agent in metal treatment, as a monomer for functional and/or biodegradable polymers, as a water softener in detergents, and as cosmetics and pharmaceuticals and for other industrial uses [14-17].

Cage compounds with several nitro groups formed a new class of high energy compounds that much attention have attracted in the last ten years. High energy density materials such as polynitropolyaza-caged compounds are candidate materials for increasing rocket, gun propellant, and explosive performance [18,19]. Hexanitrohexaazaisowurtzitane (HNIW or CL-20) was first synthesized in 1990 were reported by Nielsen [20]. Cage structure CL-20 creates

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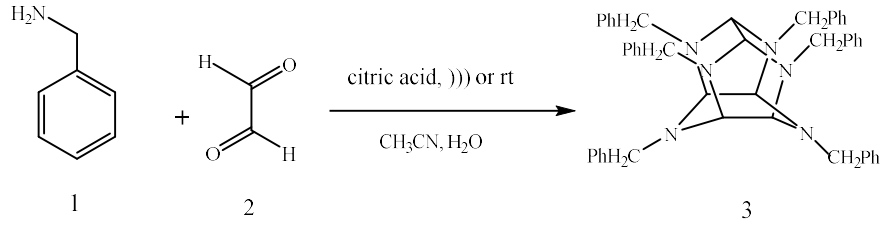
three positive parameters, as follows: i) High density, due to compression of the cage structure. ii) High heat of formation, because of polycyclic and pressure ring. iii) Good thermal stability [21,22].

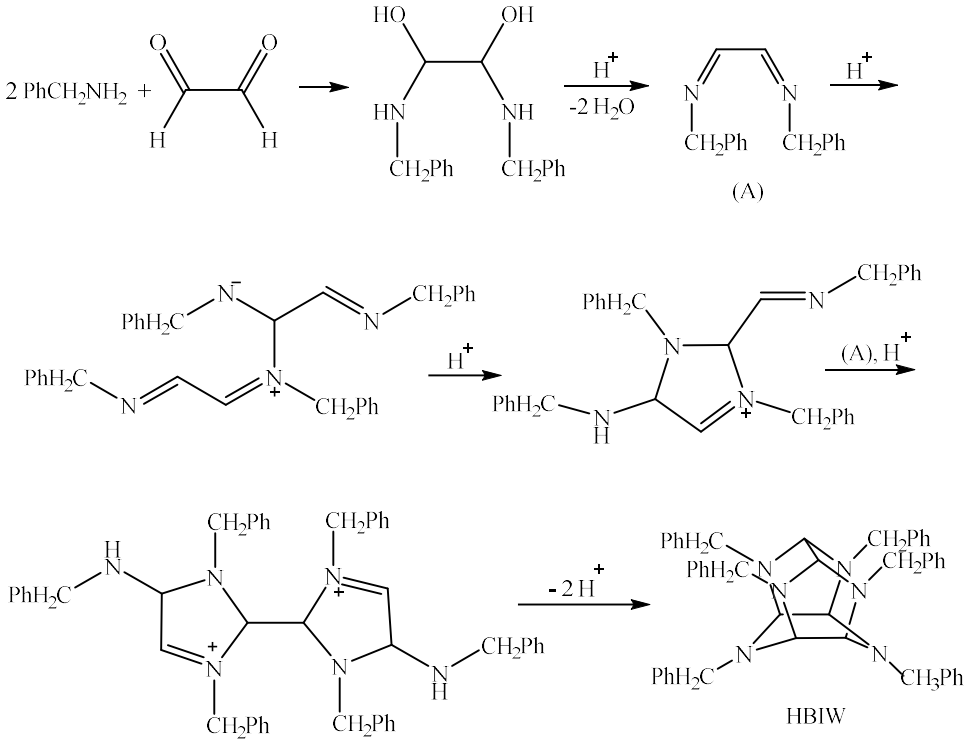
Hexabenzylhexaazaisowurtzitane (HBIW) is used as a precursor for the synthesis of HNIW. The synthesis of HBIW is remarkable because it builds a 12-atom polycyclic cage compound in a one-pot cascade reaction with three glyoxal and six benzylamines in the presence of formic acid as catalyst [18]. Formic acid has proven to be highly corrosive at concentrations over 50% especially if contaminated by acidic oxidizing chlorides. Because of its corrosive nature at high concentrations material selection can be a challenge. Formic acid is corrosive to many alloys including stainless steel, nickel alloys and zirconium. Formic acid as a reducing agent attacks stainless steel unless an oxidizing agent is added. [23,24].

Recently, Ramazani and co-workers [25] used silica nanoparticles as catalyst under ultrasonic irradiation to prepare of HBIW. Ultrasound is a highly useful method for preparation of many compounds. The advantages of this method include higher yield, shorter reaction time, and milder conditions [26-31].

The aim of the present investigation was to remove formic acid catalyst, because of its corrosive nature, and introducing a green catalyst in the synthesis of HBIW. 2,4,6,8,10,12-hexabenzyl-2,4,6,8,10,12-hexaazatetracyclo [5,5,0,^{05,9},0^{3,11}] dodecane (hexabenzyl hexaazaisowurtzitane, HBIW (**3**)), was synthesized by the easy condensation of glyoxal (**2**) with benzylamine (**1**) in acetonitrile-water as solvent which catalyzed by citric acid under ultrasound irradiation and the stirring conditions at room temperature (Scheme 1). A proposed mechanism for the synthesis of HBIW is presented in the Scheme 2.



Scheme 1. Synthesis of HBIW catalyzed by citric acid.



Scheme 2. A proposed mechanism for the synthesis of HBIW in the presence of citric acid.

2. Experimental

2.1. General

All chemicals, including benzylamine, glyoxal, citric acid, acetonitrile, ethanol, methanol, chloroform, dichloromethane, tetrahydrofuran were purchased with high purity from Fluka and Merck (Darmstadt, Germany). Melting points were determined on an Electrothermal 9100 apparatus. Infrared spectra were recorded on a Mattson (Unicam Ltd., Cambridge, UK) 1000 Fourier transform infrared spectrophotometer using KBr technique. ^{1}H NMR spectra ($CDCl_3$) were recorded on a Bruker (Karlsruhe, Germany) DRX-250 Avance spectrometer at 250.0 MHz. Sonication was performed in a Bandelin (Berlin, Germany) SONOPULS ultrasonic homogenizers with 20-kHz processing frequency, a nominal power of 250 W, and uniform sonic waves.

2.2. Typical procedure for synthesis of HBIW

Benzylamine (0.0085 mol, 0.937mL), citric acid (5% mol with respect to glyoxal), acetonitrile (7.75 mL), and water (0.775 mL) was placed in a round-bottomed flask of 100 mL. The reaction mixture was stirred at room temperature and glyoxal (40% aqueous solution; 0.00375 mol, 0.427mL) was added dropwise (15 min). Then the mixture was irradiated with ultrasound under a power of 150W for 5 min or was stirred at room temperature at a specified time. Formation of HBIW monitored by TLC.

The precipitated solid was collected by filtration then was washed with cold excess ethanol and dried under high vacuum to give the pure final product. The product can be further purified by recrystallization from ethyl acetate.

Spectral data of the product

White solid. m.p.= 154–157 ºC. FT-IR (KBr): $\bar{\nu}$= 3022, 2942, 2835, 1951, 1601, 1450, 1351, 1169, 1138, 989, 926, 836, 732, 699 cm^{-1}. ^{1}HNMR ($CDCl_3$): $\delta_=$ 7.24-7.28 (m, 30H, phenyl CH), 4.16 (s, 4H, CH_2), 409 (s, 8H, CH_2), 4.04 (s, 4H, CH), 3.57 (s, 2H, CH) ppm.^{13}CNMR ($CDCl_3$): 56.21-56.88 (6C, CH_2-phenyl), 76.51-80.64 (6C, CH (skeletal)), 126.62-140.74 (36C, phenyl) ppm.

3. Results and Discussion

3.1. Effect of catalyst amount on product yield

In order to verify the effect of catalyst amount on product yield, the reaction between benzylamine and glyoxal was done in the presence of various the amounts of catalyst. The results in Table 1 clearly show that the product yield increased with increasing the amounts of catalyst up to 5 mol%, but in the presence of more amounts of citric acid catalyst, reduction of the product yield was observed. It seems that the product hydrolysis could be occur in the presence of higher concentration of citric acid catalyst. However, in the absence of a catalyst, the reaction yielded only 17% of the product.

3.2. Effect of solvent on the product yield

The effect of different solvents on the yield of HBIW is given in Table 2. In these experiments, we observed that the reaction between benzylamine with glyoxal was solvent dependent. We found that acetonitrile was the best solvent for this reaction.

3.3. Influence of reaction time on the product yield

Since the amount of catalyst and solvent were optimized, the influence of reaction time on the reaction was studied in the next step. The effect of reaction time on the synthesis of HBIW was examined and the results are reported in the Table 3.

Table 1. Effect of the catalyst in the synthesis of HBIW.[a]

Entry	Catalyst (mol (%))	Yield[b] (%)	Yield[c] (%)
1	No catalyst	17	17
2	Citric acid (1)	60	74
3	Citric acid (3)	71	78
4	Citric acid (5)	89	87
5	Citric acid (10)	66	60

[a]Reaction conditions: benzylamine (0.0085 mol, 0.937 mL), glyoxal (0.0037 mol,0.427 mL),CH_3CN (7.75 mL), H_2O (0.775 mL), and catalyst (% mol with respect toglyoxal).
[b]Yield of product under ultrasound irradiation (5 min, 150 W).
[c]Yield of product under stirring at room temperature (24 h).

Table 2. Model reaction catalyzed by citric acid in different solvents.[a]

Entry	Solvent	Yield[b] (%)	Yield[c] (%)
1	Acetonitrile	89	87
2	Ethanol	64	58
3	Methanol	60	54
4	Chloroform	62	56
5	Dichloromethane	54	48
6	Tetrahydrofuran	58	52

[a]Reaction conditions: benzylamine (0.0085 mol, 0.937 mL), glyoxal (0.0037 mol, 0.427 mL), solvent (7.75 mL), H_2O (0.775 mL), and citric acid (5% mol with respect toglyoxal).
[b]Yield of product under ultrasound irradiation (5 min, 150 W).
[c]Yield of product under stirring at room temperature (24 h).

Table 3. Different runs for choosing the optimum duration.[a]

Entry	Time[b] (min)	Yield[b] (%)	Time[c] (h)	Yield[c] (%)
1	3	64	6	80
2	5	89	12	83
3	10	90	18	86
4	15	91	24	87
5	30	91	48	92

[a]Reaction conditions: benzylamine (0.0085 mol, 0.937 mL), glyoxal (0.0037 mol, 0.427 mL), acetonitrile (7.75 mL), H_2O (0.775 mL), and citric acid (5% mol with respect toglyoxal).
[b]Ultrasound irradiation (150W).
[c]Stirring at room temperature.

3.4. Influence of ultrasound power on the product yield

In order to verify the effect of irradiation power, the reaction was also performed at 50, 100, 150, and 200 W. By increasing the irradiation power from 50 to 150W, the yield increased from 58 to 89% (Table 4). The best yield for HBIW was obtained by ultrasonic irradiation for 5 min at room temperature and 150W.

4. Conclusions

In this study, we have reported citric acid as a green catalyst for the preparation of hexabenzylhexaazaiso-wurtzitane (HBIW) under both conventional stirring and ultrasonic irradiation conditions. In general, improvements in rates and yield of the reactions were observed by carrying out the reactions under ultrasound irradiations.

Acknowledgment

This work was supported by the "*Iran National Science Foundation: **INSF***".

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