SIMPLE, NOVEL SYNTHESIS OF FURFURYLAMINE FROM FURFURAL BY ONE-POT REDUCTIVE AMINATION IN WATER USING ZINC METAL

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ABSTRACT: A novel, environmentally eco-friendly and high yielding method for the preparation of furfurylamine by one-pot reductive amination of furfural is reported. The reaction is carried out using hydroxylammonium chloride as amination agent and cheap zinc powder as reducer in the presence of zinc chloride and ammonium chloride. This practical procedure has been carried out in water and in neat conditions.

Key words: Renewable resources, furfurylamine, sustainable chemistry, zinc, reduction

RESUME: Un nouveau procédé non polluant est proposé pour préparer avec de bon rendement la furfurylamine en une seule étape par amination réductrice du furfural. La réaction est réalisée en utilisant le chlorure d'hydroxylammonium comme agent d'amination et une poudre de zinc comme réducteur, en présence de chlorure de zinc et de chlorure d'ammonium en milieu aqueux.

Mots clés: Les ressources renouvelables, furfurylamine, zinc, réduction

INTRODUCTION

The process for refining renewable nonfood biomasses of vegetable origin developed by CIMV (www.cimv.fr)[1-4] offers a new alternative to chemical industry since it allows the mass production of cellulose, lignin and hemicelluloses (C5 and C6 sugars). The C5 sugars, the third most abundant and renewable material on earth after cellulose and lignin can be refined. After the removal of tannins and proteins, the cyclodehydration of C5 sugars allows to obtain furfural[5-8] with yields up to 83 %[8].

Their high-yield production by clean and sustainable processes promoted the emergence of Agrichemistry (chemistry of the renewable molecules) which will eventually counter-balance the omnipotence of Petrochemistry (chemistry of the fossil molecules). Therefore, Agrichemistry has a major role to play in sustainable development[4].

The chemistry of furfural provides new opportunities for the synthesis of furanic compounds like furfurylamine and derivatives. A high-yield production of furfurylamine and derivatives can allow to replace benzylamine and derivatives on an industrial scale for the manufacturing of agriculture fertilizers[9], pharmaceutical drugs[10], and polymers with high-performance[11] and biodegradable[12] properties.

The existing process for producing furfurylamine involves reacting furfural with ammonia and hydrogen gas using Pd-C or Raney nickel as hydrogenation catalyst[13-16]. This reaction is carried out in an anhydrous solvent under high pressure[15]. However, due to the high investment needed for the high-pressure reactors and expensive catalysts, this method is not attractive. Furthermore,

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little consideration has been given to environmental and safety concerns. Therefore, this process is not suitable for the mass production of furfurylamine.

Alternatively, furfurylamine can be prepared through various other methods. Among these, the reductive amination remains one of the most versatile and useful synthetic routes which is generally based on the conversion of carbonyls to imines or oximes followed by a reduction reaction. While the reduction of imines is not selective and can lead to secondary or tertiary amines[15-19], primary amines are selectively produced from the reduction of oximes.

Recently, there has been a growing interest in the use of more environmentally friendly chemical synthetic procedures under organic solvent-free conditions. In this concern, we have developed here a simple, original and high yielding greener protocol for the synthesis of furfurylamine. We studied in detail the conversion of furfural to the corresponding furfurylamine using $H_2NOH.HCl/Na_2CO_3$ and $Zn/NH_4Cl/ZnCl_2$ systems and only water as solvent.

EXPERIMENTAL

General: All chemistry reagents were purchased from Acros Organics and Fisher chemical. Commercially available starting reagents were used without further purification. All compounds were analyzed with a PerkinElmer Spectrum 100 Universal ATR-FTIR (Attenuated Total Reflectance-Fourier Transform InfraRed analysis) instrument equipped with a diamond/ZnSe crystal single reflection. The ^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded on a Bruker Avance 300 spectrometer at 25°C using $CDCl_3$ as solvent.

Synthesis of Furfuryloxime: To a mixture of furfural (10mL, 120.72mmol) and hydroxylammonium chloride (10.07g, 144.86mmol) in water (20 mL) was added drop-wise a solution of sodium carbonate (7.68g, 72.43mmol) in water (30ml). Then, the resultant solution was stirred at room temperature for 3h. After the mixture was filtered, furfuryloxime was collected as a brown solid in quantitative yield (13.33g).

Synthesis of furfurylamine by Zn/HCl system: To a solution of furfuryloxime (2g, 18mmol) in hydrochloric acid (6.0M, 24ml) was added drop-wise zinc dust (4.71g, 72mmol), and the resultant solution was stirred at room temperature for 2 h. To the resulting slurry was added drop-wise a solution of ammonia (30%, 5.1 mL) and sodium hydroxide (6M, 24mL), the mixture was heated to 60° and stirred for 15mn. After, the resultant solution was cooled and filtered. Then, the mother liquid was extracted with cyclohexane, dried over anhydrous sodium sulfate and filtered. The solvent was removed under vacuum to afford the furfurylamine as a yellow liquid without further purification in 96% of yield (1.68g). The purity determined by NMR was found to be superior to 95%.

Synthesis of furfurylamine by Zn/NH_4Cl system: To a stirred mixture of furfuryloxime (2g, 18mmol), NH_4Cl (4.81g, 90mmol) and water (12mL) at 60°C was added zinc dust (8.24g, 126mmol) and $ZnCl_2$ (0.24g, 3.6mmol). After the reaction mixture was stirred for 15mn at 60°C, the insoluble materials were filtered off. Then, to the mother liquid was added a solution of sodium hydroxide (6M, 15mL). The aqueous layer was extracted with cyclohexane, and the organic layer was dried over anhydrous sodium sulfate and filtered. The solvent was evaporated in vacuo to give the furfurylamine as a yellow liquid without further purification in 99% of yield (1.74g). The purity determined by NMR was found to be superior to 95%.

One-pot synthesis of furfurylamine: Furfural (10mL, 120.72mmol) and hydroxylammonium chloride (10.07g, 144.86mmol) were mixed in water (20 ml) and then, a solution of sodium carbonate (7.68g, 72.43mmol) in water (30mL) was added drop-wise. After completion of the furfuryloxime formation, the resultant solution was heated to 60°C, then H_2O (33 mL), zinc dust (55.27g, 845.04 mmol), NH_4Cl (32.29g, 603.6 mmol) and $ZnCl_2$ (1.64g, 12.07mmol) was added. The mixture was stirred for 15mn. After cooling and filtration, the unreacted zinc was recovered from the reaction mixture (35.85g, 548.07mmol). Then, to the mother liquid was added a solution of sodium hydroxide (6M, 100mL). The aqueous layer was extracted with cyclohexane, and the organic layer was dried over anhydrous sodium sulfate and filtered. The solvent was removed under vacuum to afford the furfurylamine as a yellow liquid without further purification in 98% of yield (11.53g). The purity determined by NMR was found to be superior to 95%.

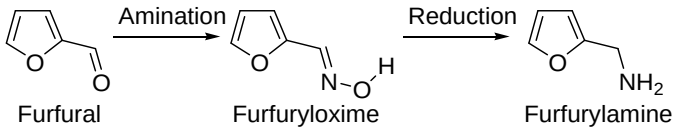
Furfurylamine/zinc complex Brown liquid; IR: 3379, 3298, 3115, 2915, 2855, 1600, 1504, 1339, 1213, 1147, 1069, 1006, 917, 883, 862, 802, 731 cm^{-1}; ^{1}H NMR (300MHz, $CDCl_3$) δ= 1.90 (s, 2H; NH_2), 3.72-3.75

(m, 2H; CH_2), 6.08-6.14 (m, 1H; CH), 6.25 (m, 1H; CH), 7.29-7.13 (m, 1H; CH); ^{13}C NMR (75 MHz, $CDCl_3$) δ= 39.2, 44.9, 105.1, 107.2, 110.1, 110.2, 141.5, 141.9, 153.4, 156.6 ppm.

Free Furfurylamine Yellow liquid; IR: 3379, 3298, 3115, 2915, 2855, 1600, 1504, 1339, 1213, 1147, 1069, 1006, 917, 883, 862, 802, 731 cm^{-1}; ^1H NMR (300MHz, $CDCl_3$) δ= 1.30 (s, 2H; NH_2), 3.62 (s, 2H; CH_2), 5.95 (m, 1H; CH), 6.13 (m, 1H; CH), 7.17 (m, 1H; CH); ^{13}C NMR (75 MHz, $CDCl_3$) δ= 39.2, 104.8, 110.0, 141.3, 156.8 ppm.

RESULTS AND DISCUSSION

Our work is based on a one-pot, two-step reductive amination (Scheme 1).



Scheme 1. Schematic production route of the furfurylamine

First, we studied in detail the two reaction steps separately in order to determine the suitable conditions for one-pot reaction.

Synthesis of furfuryloxime

The first step involves the synthesis of furfuryloxime. It is generally carried out by reacting furfural with hydroxylammonium chloride in the presence of a base in aqueous, organic or hydro-organic media[20-23]. Recently, Liu and co-workers[21] showed that this reaction can be completed in one hour stirring in boiling water in the presence of hydroxylammonium chloride and sodium carbonate using a Furfural/$H_2NOH.HCl$/Na_2CO_3 molar ratio of 1/1.4/0.5. The crude furfuryloxime can be obtained by simple filtration after cooling. This method presents the advantage of the use of an aqueous media.

We repeated this reaction using the same conditions and observed the total conversion of furfural. However, the resulted product was not pure. This result is not surprising, as oximes can transform to different products in acid media at elevated temperatures[24-26]. Therefore, we recrystallized the resulted product from water to obtain the pure furfurylamine with a yield of 80 % (m.p. 78°C).

Additionally, at the corresponding reaction temperature, the precipitation of the furfuryloxime can take several hours. In order to avoid these drawbacks, we carried out the reaction:

- in a neutral media with Furfural/$H_2NOH.HCl$/Na_2CO_3 molar ratio of 1/1.2/0.6,
- at room-temperature. Under these conditions, furfuryloxime precipitates during the reaction and is isolated quantitatively by simple filtration only after 3 hours at the end of the reaction.

Being encouraged by this result, we proceeded to the next step which involves the reduction of furfuryloxime to furfurylamine.

Synthesis of furfurylamine

The reduction of oximes can be carried out by various methods other than catalytic hydrogenation. Generally two methods are used:

- One employs metal hydrides such as $NaBH_4$[27], $NaBH_3(CN)$[17] and $LiAlH_4$[22,28,29]. However, it requires expensive reagents and should be most of the time carried out in anhydrous conditions.
- In the second method, the oxime is reduced in a metal-acid system such as Zn/AcOH[18,21,23,30] or Zn/HCO_2H[32] through hydrogen radical formation. The radicals are produced from the reaction of the protons with the metallic zinc ($2H^+ + Zn \rightarrow 2H^{\bullet} + Zn^{2+}$). This method is somehow better than the

others but involves the use of large excess of acid and many purification steps. However, when we attempted to synthesize furfurylamine using this procedure, the expected product degraded during the evaporation process of the acetic acid at the end of the reaction. Furthermore, during the reaction, the amine formed can react with the carbonyl of the acid compound to form an amide.

In order to overcome these problems, we modified the Zn-acid system. We used HCl as the acidic reagent and optimized the reaction conditions by varying the molecular equivalents of the reagents while keeping the temperature constant at room-temperature, except for the experiment in entry 10 which was conducted at a much lower temperature because of the exothermic reaction due to the high concentration of HCl added (Table I).

Table I. Influence of zinc dust and Hydrochloric acid on the reduction reaction[a]

Runs	Zn (equiv)	[HCl]	HCl (equiv)	T(°C)	Time (h)	Yield[b] (%)
1	7	0.1	1	25	72	10
2	7	0.1	2	25	72	19
3	7	0.1	4	25	72	53
4	7	0.1	7	25	72	87
5	7	0.1	8	25	72	98
6	5	0.1	8	25	72	98
7	4	0.1	8	25	72	98
8	3	0.1	8	25	72	79
9	4	6	8	25	2	98
10	7	12	8	-10	1.5	98

[a]Furfuryloxime: 1 (equiv), Solvent : H_2O, [b]Isolated yields.

The results presented in the table show that using the proper Zn/HCl ratio and good acid concentration allows the quantitative synthesis of furfurylamine in water at room temperature. Using 1 equivalent of furfuryloxime, 4 equivalents of zinc and 8 equivalents of hydrochloride acid at 0.1 M (Table I, Run 7) yielded quantitatively furfurylamine after 3 days of reaction. The use of a more concentrated acidic media reduces significantly the reaction time to 2 hours at room temperature (Table I, Run 9).

Despite the quantitative yields obtained, this method presents some drawbacks including: (i) the formation of a complex between the furfurylamine and the Zn^{2+}, (ii) the use of a large excess of zinc.

(i) The complex formation between the furfurylamine and Zn^{2+} is due to the formation of a coordinate bond between the electron pair of the nitrogen and the empty valance orbital of the Zn^{2+} ion. The coordinated and non-coordinated furfurylamine give the similar IR spectra however, ^{1}H and ^{13}C NMR spectra show shifts in all the peaks and doubling in some (figure 1, 2). This phenomenon is attributed to the presence of a furfurylamine complex. A similar interpretation was made for benzylamine in another study[32]. Based on this study, we can conclude furfurylamine is coordinated to the Zn^{2+} metal center. The furfurylamine can be liberated from the complex by the addition of a mixture of ammonia and caustic soda. The ammonia breaks the furfurylamine complex by bonding to Zn^{2+} to form an ammonia/Zn^{2+} complex.

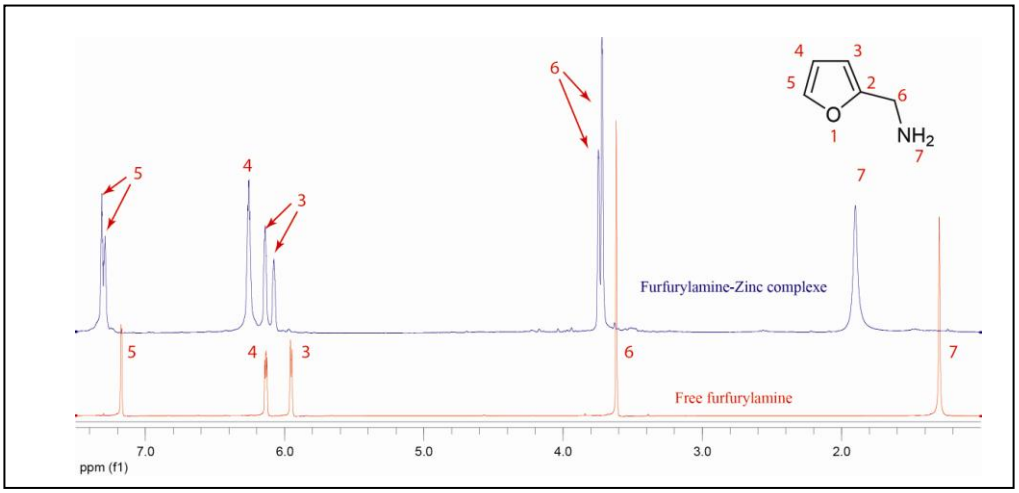


Figure 1. The ^{1}H NMR spectrum of Furfurylamine-Zinc complex and free Furfurylamine in $CDCl_3$.

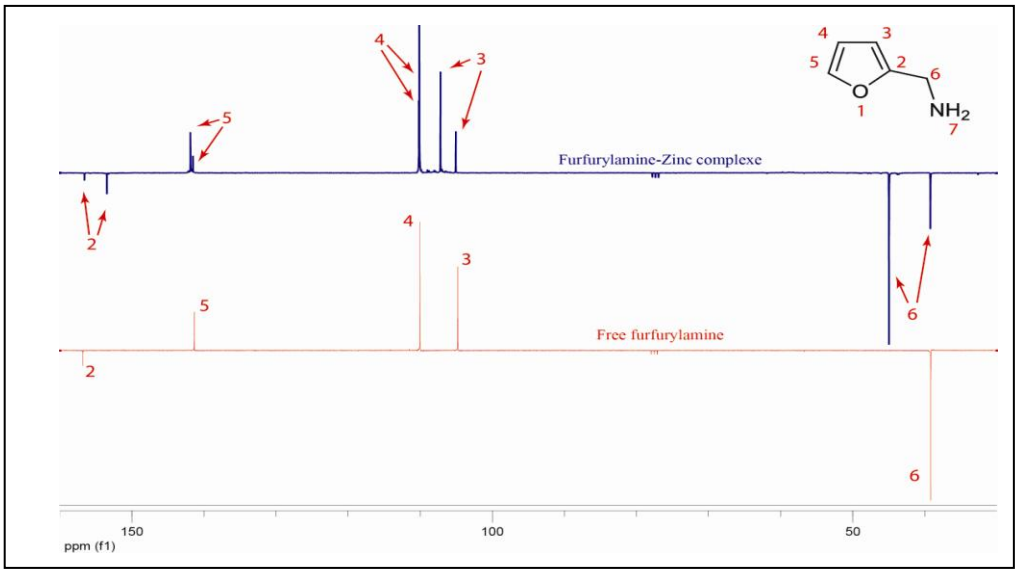
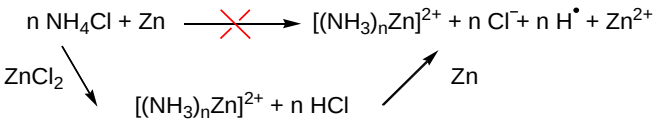


Figure 2. The ^{13}C DEPT-135 spectrum of Furfurylamine-Zinc complex and free Furfurylamine in $CDCl_3$.

(ii) The formation of hydrogen radicals during the reduction of furfuryloxime is due to the high reactivity of the metallic zinc. If the radical concentration is high enough in the reaction media, along with the reduction of furfuryloxime, dihydrogen formation takes place. Therefore, the complete reduction of furfuryloxime requires the use of excess zinc and acid.

In order to avoid the addition of excess amounts of reagents, we replaced the hydrochloric acid, which is a strong acid that dissociates completely, with ammonium chloride. Our preliminary attempts to conduct the reduction of furfuryloxime with the NH_4Cl/Zn system in different solvents and at different temperatures failed (Table II, Runs 1-6). This is probably due to the absence of the free protons in the reaction media. In order to favor the reaction, we took advantage of the high affinity of amines towards Zn^{2+} (Table II, Runs 7-12). NH_4Cl produces HCl upon reacting with $ZnCl_2$ and the in-situ formed HCl, then, reacts with the zinc metal to give hydrogen radicals, as well as new Zn^{2+} ions (Scheme 2).



Scheme 2. Production of hydrogen radicals with $Zn/NH_4Cl/ZnCl_2$ system.

Upon addition of $ZnCl_2$ in the reaction media, we obtained furfurylamine in different yields. As a solvent, water was superior to ethanol and THF in terms of reaction time and yield (Table II, Runs 8,10,12). We obtained furfurylamine in quantitative yield using 0.1 equivalent of $ZnCl_2$ in only one hour at 60 °C (Table II, Run 12).

Table II. Influence of solvent and zinc chloride on the reduction reaction[a]

Runs	$ZnCl_2$ (equiv)	Solvents	Time (h)	T(°C)	Yield[b] (%)
1	0	EtOH	2	25	0
2	0	EtOH	2	60	0
3	0	THF	2	25	0
4	0	THF	2	60	0
5	0	H_2O	2	25	0
6	0	H_2O	2	60	0
7	0.1	EtOH	2	25	9
8	0.1	EtOH	2	60	47
9	0.1	THF	2	25	4
10	0.1	THF	2	60	39
11	0.1	H_2O	2	25	23
12	0.1	H_2O	1	60	98

[a]Furfuryloxime: 1 (equiv), Zn: 5 (equiv), NH_4Cl: 2 (equiv), [b]Isolated yields.

Two equivalents of NH_4Cl were necessary for the total conversion of the furfuryloxime to furfurylamine. However, using these ratios, the purification of furfurylamine is difficult as it is not in the free form. Increasing the NH_4Cl to furfuryloxime ratio to 4 or more allows the isolation of free furfurylamine. In fact, the affinity of ammonium towards Zn^{2+} limits the coordination between Zn^{2+} and furfurylamine.

We observed that the quantity of zinc used influences not only the reduction of furfurylamine but also the reaction time. The latter decreases as the quantity of Zn added increases. For example, using 7 equivalents of zinc metal decreases the reaction time from 2 ½ hours to 15 mn compared to 3 equivalents (Table III, Run 2,6). However, adding more than 7 equivalents does not have any influence on the reaction time. In fact, while only 2.5 equivalents of zinc are necessary for the reduction of furfuryloxime, the excess is used to accelerate the reaction. The use of excess zinc is not a big drawback as the unreacted zinc can be recovered from the reaction mixture by simple filtration.

We also investigated the effect of the operating temperature on the reduction of furfuryloxime. We found that the latter is controlled thermodynamically. Indeed, while it takes 24 hours for the reaction to complete at 20°C, it is completed in 15 minutes at 60°C. Above this temperature, we did not observe any difference in the reaction time.

Table III. Influence of zinc metal on the time reaction[a]

Runs	Zn (equiv)	Time (mn)	Yield[b] (%)
1	2	180	87
2	2.5	180	98
2	3	150	98
3	4	110	98
4	5	60	98
5	6	25	98
6	7	15	98
7	8	15	98

[a]Furfuryloxime: 1 (equiv), $ZnCl_2$: 0.1 (equiv), NH_4Cl: 2 (equiv). T: 60°C, Solvent : H_2O, [b]Isolated yields.

One-pot synthesis of furfurylamine

After having studied each formation step of furfurylamine from furfural, we observed the similarity of the operative conditions in every case. Therefore, the two steps should be able to be carried out *in-situ* without isolating the furfuryloxime intermediate. In fact, we have successfully carried out the synthesis of furfuryloxime and its subsequent reduction to furfurylamine in one-pot by introducing successively the amination and reduction reagents into the aqueous reaction medium. For the first step, we used furfural/H_2NOH.HCl/Na_2CO_3 molar ratio of 1/1.2/0.6 and room temperature to obtain furfuryloxime, and by the subsequent addition of Zn into the reaction medium using the same conditions as in Table III (Run 6), we obtained furfurylamine with the same yield (98 %) as that obtained from two separate reactions. The advantages of one-pot reaction are that the number of unit operations is decreased and the amount of effluents is reduced.

CONCLUSION

In conclusion, we have developed a highly efficient and ecofriendly method for one-pot reductive amination of furfural to afford furfurylamine, a promising renewable building block. This procedure has some advantages over other methods since the reaction is carried out using hydroxylammonium chloride/Na_2CO_3 as amination agent and cheap zinc powder/NH_4Cl/$ZnCl_2$ as reducer. Both of the two reaction steps are carried out in water without any organic solvents under mild conditions to afford the corresponding furfurylamine in quantitative yields. We will further investigate this method for the synthesis of a wide range of primary amines which can find potential application in the chemical and pharmaceutical industry.

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