

ZrOCl₂·8H₂O as a highly efficient, eco-friendly and recyclable Lewis acid catalyst for one-pot synthesis of *N*-substituted pyrroles under solvent-free conditions at room temperature

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A new and efficient method for the synthesis of a variety of *N*-substituted pyrroles from condensation reactions of 2,5-hexanedione with amines or diamines using ZrOCl₂·8H₂O as a water-tolerant Lewis acid catalyst at room temperature is described. The use of nontoxic, inexpensive, easily available and reusable catalyst under solvent-free conditions make this protocol practical, environmentally friendly and economically attractive. Copyright © 2011 John Wiley & Sons, Ltd.

Keywords: pyrroles; solventless reaction; ZrOCl₂·8H₂O; Paal–Knorr reaction; amine

Introduction

Pyrrole frameworks have attracted a plethora of research areas owing to the broad applications as pharmaceutical agents,^[1,2] conducting polymers,^[3] molecular optics,^[4,5] electronics,^[6] gas sensors for organic compounds^[7] and many physiologically interesting natural products as building blocks, such as alkaloids.^[8] In particular, substituted pyrroles present antibacterial,^[9] antiviral,^[10] anti-inflammatory and antioxidant activities.^[11] Owing to the multiple uses and varieties of biological activities, the synthesis of this ring system has been the subject of intense investigation. The classical methods of constructing pyrrole ring systems include mainly Hantzsch and Knorr or Paal–Knorr syntheses, which have been reported in many research articles.^[12–14] Among these methods, the most reliable, commonly used and straightforward approach for the preparation of substituted pyrrole derivatives is the Paal–Knorr reaction, which consists the cyclocondensation of primary amines with 1,4-dicarbonyl compounds and their masked equivalents. A variety of acidic materials, such as zeolite,^[15] Ti(OPrⁱ)₄,^[16] Al₂O₃,^[17] *p*-TSA,^[18] H₂SO₄,^[19] I₂,^[20] KSF, Fe⁺³-montmorillonite,^[20] HCl,^[21] montmorillonite K10,^[22] Sc(OTf)₃,^[23] Bi(NO₃)₃·5H₂O,^[24] RuCl₃,^[25] InCl₃,^[26] SnCl₂·2H₂O,^[27] layered zirconium phosphate and sulfophenyl phosphonate^[28] and others^[29] have been used to promote these condensations. Additionally, the above cyclocondensation process could proceed in ionic liquid^[30] or ultrasonic and microwave irradiation.^[31] However, despite the potential utility of the aforementioned routes for the synthesis of substituted pyrrole derivatives, some of them involve the use of excess amounts of acids because they can be trapped by nitrogen in this condensation, or hazard organic solvents, tedious work-up leading to the generation of large amounts of toxic metal-containing waste, large amounts of solid catalysts, and so they may not be the preferred choices in view of the requirements of green chemistry. Moreover, low yields, long reaction times, and the use of expensive reagents are other disadvantages of some of the reported methods. Therefore, to avoid these limitations, the discovery of a new and efficient catalyst with high catalytic activity, short reaction time, recyclabil-

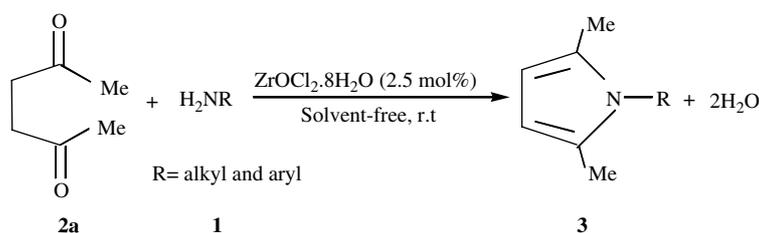
ity and simple work-up for the preparation of substituted pyrroles by the Paal–Knorr condensation under neutral, mild and practical conditions is of prime interest.

Lewis acid-catalyzed reactions receive great attention because of their unique reactivity and selectivity, and the mild conditions used.^[32] Most zirconium (IV) compounds have relatively low toxicity, are easy to handle, have low cost and possess good stability. Zr⁴⁺ has a high charge-to-size ratio (Z^2/r , 22.22 e² m⁻¹⁰) and for this reason, zirconium (IV) compounds possess a high coordinating ability that allows strong Lewis acid behavior and high catalytic activity.^[33] With increasing environmental concerns and the need for efficient and green Lewis acid catalysts for various useful organic transformations, the interest in zirconium compounds has increased in the last decade. Among Zr (IV) compounds, ZrOCl₂·8H₂O has been shown to be different from traditional Lewis acids such as AlCl₃, SnCl₂ and BF₃·OEt₂, and is also quite stable in water, nontoxic, reusable, readily available and inexpensive as well as highly effective in the case of many nitrogen containing compounds such as nitriles and amines.^[34] ZrOCl₂·8H₂O is an oxysalt of Zr and its handling is easier in comparison to that of the moisture-sensitive ZrCl₄. In recent years, several important organic transformations using this catalyst have been reported in the literature.^[35–41]

In continuation of our interest in the synthesis of organic compounds from condensation of phenols with dialdehydes, especially, 2,5-dimethoxytetrahydrofuran as a protected 1,4-dicarbonyl compound,^[42] and our ongoing research on the application of heterogeneous solid acid catalysts for development of useful synthetic methodology,^[43] herein we wish to report an efficient and eco-friendly method for the synthesis of pyrroles by

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**Scheme 1.**

the condensation of 2,5-hexanedione with primary amines in the presence of a catalytic amounts of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ as the catalyst at ambient temperature under solvent-free conditions in good to excellent yields with rather short reaction times (5–40 min; Scheme 1).

Experimental Section

Materials and Methods

All chemical reagents and $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ were obtained from Fluka and Merck Chemical Companies and were used without further purification. Melting points were measured on an Electrothermal 535 apparatus and were uncorrected. ^1H , ^{13}C NMR spectra were recorded on a Bruker DPX-250 Avance spectrometer at 250.13 MHz. IR spectra were recorded on a Unicam Matteson 1000 spectrophotometer. Reaction monitoring and purity determination of the products were accomplished by TLC on silica gel polygram SILG/UV₂₅₄ plates. All yields refer to isolated products. Elemental analyses were performed using a Heraeus CHN-O-Rapid analyzer by RIPI and the results agreed favorably with calculated values.

General Synthetic Procedure for the Preparation of *N*-Substituted Pyrroles

To a mixture of amine **1** (1 mmol) and 2,5-hexanedione **2a** (1 mmol) was added $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ (2.5 mol%). The mixture was stirred at room temperature for the appropriate time according to Table 2. The progress of the reaction was monitored by TLC (eluent: *n*-hexane–ethyl acetate, 3:1). After completion of the reaction, EtOAc (10 ml) was added. The mixture was filtered and the catalyst was washed with EtOAc (10 ml). The filtrate was evaporated under reduced pressure and the residue was purified by short silica gel column or by recrystallization to afford the pure product. All the pyrrole products are known compounds and were characterized by IR and NMR spectroscopies data and their melting points, which agreed with reported values.^[20,24,26,29,30,45,46]

Results and Discussion

At the onset of this work, we investigated a variety of conditions with the model reaction involving aniline **1a** (1 mmol) and 2,5-hexanedione **2a** (1 mmol) using $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ as catalyst to afford the pyrrole product **3a**. The results are summarized in Table 1. The best results were obtained by carrying out the model reaction at room temperature for 15 min with 2.5 mol% of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ catalyst without any solvent, and the reaction in the different solvents examined, such as CH_2Cl_2 , CHCl_3 , THF, CH_3OH , EtOAc, and CH_3CN , took longer times than in neat conditions. In addition,

Table 1. The condensation reaction of 2,5-hexanedione (**2a**) with aniline (**1a**) under different reaction conditions at room temperature

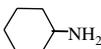
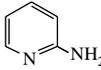
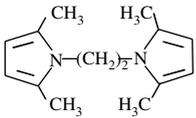
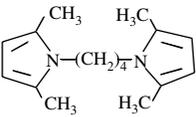
Entry	Solvent ^a	Time (min)	Yield ^b (%)
1	CH_2Cl_2	35	70
2	CHCl_3	35	69
3	THF	45	60
4	CH_3CN	35	73
5	CH_3OH	40	62
6	EtOAc	35	68
7	None (no catalyst)	6 h	Trace
8	None ($\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$, 1 mol%)	30	79
9	None ($\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$, 2 mol%)	25	86
10	None ($\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$, 2.5 mol%)	15	93
11	None ($\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$, 3.5 mol%)	15	93

^a The reaction was carried out using 2.5 mol% of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ in 3 ml of solvent at room temperature.

^b Isolated yield.

we also studied the influence of the amount of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ on the reaction yields. We found that the yield was not significantly affected by adding different amounts of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ catalyst, and excessive amount of catalyst did not increase the yield remarkably (Table 1, entry 11). To illustrate the need for $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ for this condensation, we examined the model reaction in the absence of catalyst. In this case the reaction did not proceed even after 6 h (Table 1, entry 7). Obviously, $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ is an important component of the reaction. In the light of this, subsequent studies were carried out in the following optimized conditions: with 2.5 mol% catalyst at room temperature in the absence of solvent (Table 1). Owing to the good results obtained, we applied the optimal protocol to a variety of amines and the results are summarized in Table 2. As indicated in Table 2, in all cases, the $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ -catalyzed Paal–Knorr condensation reaction proceeded smoothly, completed within 5–40 min, gave the corresponding pyrrole products in good to excellent yields, and also avoided the problems associated with solvent use, such as cost, handling, safety and pollution. Different kinds of aromatic amines bearing either electron-donating (Table 2, entries 2–4 and 6) or electron-withdrawing (Table 2, entries 5 and 7) groups on aromatic rings were converted to the corresponding *N*-substituted pyrroles in the presence of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$. Both cyclic and acyclic aliphatic amines gave excellent yields of the desired pyrroles (Table 2, entries 12 and 8–11). It is well known that aliphatic amines possess a greater reactivity compared with aromatic amines; thus aliphatic amines give higher yields or shorter reaction times than are generally observed in other systems.^[44] Moreover, we also examined the reactivity of less nucleophilic aromatic amines such as 1-aminonaphthalene with **2a** in the presence of

Table 2. ZrOCl₂·8H₂O-catalyzed synthesis of pyrroles under solvent-free conditions^a

Entry	Amine (1)	Product (3)	Time (min)	Yield ^b (%)	Reference
1	C ₆ H ₅ NH ₂	3a	15	93	[24, 26]
2	<i>p</i> -(CH ₃)C ₆ H ₄ NH ₂	3b	15	92	[24,26]
3	<i>o</i> -(CH ₃)C ₆ H ₄ NH ₂	3c	15	91	[24,30]
4	<i>p</i> -(OCH ₃)C ₆ H ₄ NH ₂	3d	10	95	[24,26]
5	<i>p</i> -(NO ₂)C ₆ H ₄ NH ₂	3e	30	87	[24,26]
6	<i>p</i> -(OH)C ₆ H ₄ NH ₂	3f	10	95	[24,30]
7	<i>p</i> -(Cl)C ₆ H ₄ NH ₂	3g	15	93	[24,26]
8	C ₆ H ₅ CH ₂ NH ₂	3h	5	97	[24,29]
9	<i>p</i> -(OCH ₃)C ₆ H ₄ CH ₂ NH ₂	3i	8	96	[24,26]
10	CH ₃ CH ₂ CH ₂ NH ₂	3j	5	97	[30]
11	CH ₃ (CH ₂) ₃ NH ₂	3k	6	97	[30]
12		3l	8	96	[30]
13		3m	40	89	[23,24]
			60	85	[20]
			660	83	[20]
			660	83	[24]
14		3n	30	89	[23,29]
15	NH ₂ (CH ₂) ₂ NH ₂	 3o	6	96	[26,29]
16	NH ₂ (CH ₂) ₄ NH ₂	 3p	8	95	[26,29]
17	C ₆ H ₅ CONH ₂	3q	40	86	[45]
18	<i>p</i> -(OCH ₃)C ₆ H ₄ CONH ₂	3r	25	90	[45]
19	C ₆ H ₅ SO ₂ NH ₂	3s	85	83	[46]
20	<i>p</i> -(OCH ₃)C ₆ H ₄ SO ₂ NH ₂	3t	80	85	[46]

^a Reaction conditions: amine (**1**, 1 mmol); 2,5-hexanedione (**2a**, 1 mmol); ZrOCl₂·8H₂O (2.5 mol%); room temperature; solvent-free.

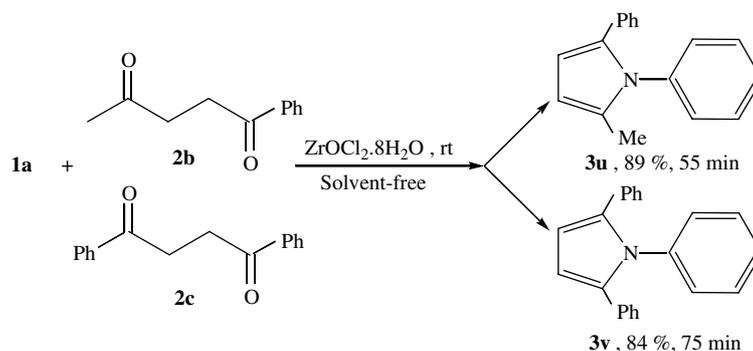
^b Isolated yield.

ZrOCl₂·8H₂O (Table 2, entry 13). The results show that this catalyst provides higher yields in shorter reaction times in comparison to the previously reported methods using I₂,^[20] montmorillonite KSF^[20] and Bi(NO₃)₂·5H₂O^[24] (Table 2, entry 13). That means that a better yield was obtained in a shorter time. Furthermore, the reactivity of heteroaromatic amine (2-aminopyridine, **1n**) with **2a** was studied (Table 2, entry 14) and it exhibited analogous behavior to the aromatic and aliphatic amines. Next, to extend the scope of the ZrOCl₂·8H₂O-catalyzed method of pyrrole synthesis, we investigated the reaction of diamines with **2a** in the same conditions (Table 2, entries 15 and 16). In this reaction, 2 equivalents of **2a** were required in order to obtain a complete conversion of diamines. When aliphatic diamines such as ethylene diamine and butylene diamine were examined, the corresponding bis-pyrrole products (**3o**, **3p**) were obtained in 96 and 95% yields, respectively. This method was also applicable to primary aromatic amides and primary aromatic sulfonamides such

as benzamide, 4-methoxybenzamide and benzenesulfonamide, 4-methoxybenzenesulfonamide (Table 2, entries 17–20) under identical reaction conditions to afford the corresponding *N*-acyl pyrroles and *N*-sulfonyl pyrroles (**3q**, **3r** and **3s**, **3t**) in good yields, respectively.

To further extend the scope and utility of this ZrOCl₂·8H₂O-catalyzed procedure of pyrrole formation, other substituted diketones such as 1-phenylpentane-1,4-dione (**2b**) and 1,4-diphenylbutane-1,4-dione (**2c**) were used. Under identical conditions, formation of pyrroles (**3u**, **3v**) was observed with **2b**, **2c** as the diketone components (Scheme 2). However, the formation of **3r** from **2c** required longer time.

The reusability of the catalyst is important from the large-scale synthesis and industrial points of view. Therefore, the recovery and reusability of ZrOCl₂·8H₂O were examined. The catalyst can be separated and reused after washing with CHCl₃ and drying at 70 °C. The reusability of the catalyst was investigated in the



Scheme 2.

Table 3. Reusability of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ catalyst in the reaction of aniline (**1a**) with 2,5-hexanedione (**2a**) under solvent-free conditions

Run	Time (min)	Yield ^a (%)
1	15	93
2	15	92
3	15	92
4	15	91
5	15	90

^a Isolated yield.

reaction of aniline with 2,5-hexanedione (entry 1, Table 2) using 2.5 mol% $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$. The results illustrated in Table 3 show that the catalyst can be used at least five times without any appreciable loss in its activity.

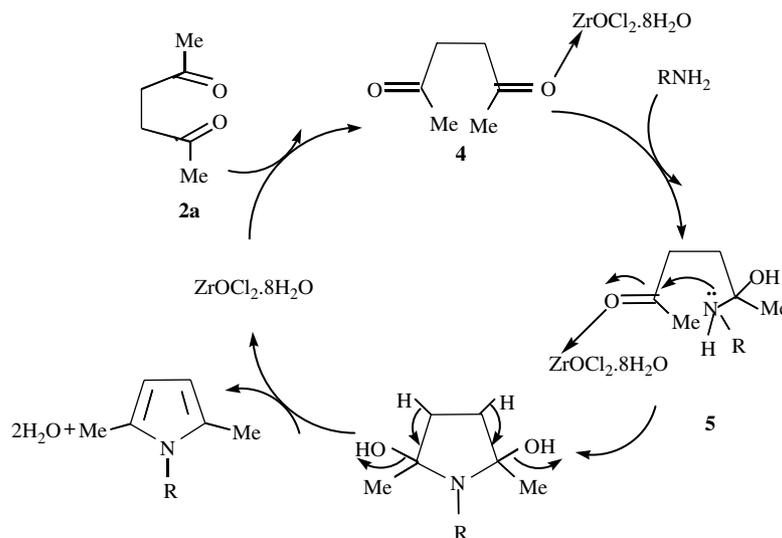
The actual mechanism of the reaction is unclear. However, the proposed mechanism for the formation of *N*-substituted pyrroles in the presence of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ as a catalyst is shown in Scheme 3. The 2,5-hexanedione (**2a**, carbonyl groups) is first activated by Zr(IV) as a Lewis acid to give **4** and then the primary amine attacks **4**, affording intermediate **5**. Cyclization and dehydration-aromatization of **5** afford the final product together with the two

H_2O molecules and release of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ for the next catalytic cycle.

Finally, to show the efficiency of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ in comparison with previously reported procedures in the literature, Table 4 compares our method with some other catalysts used in the synthesis of (**3h**, **3a**) from benzyl amine, aniline (**1h**), (**1a**) and 2,5-hexanedione (**2a**) with respect to reaction times and yields of obtained products. It is clear from the results shown in Table 4 that condensation reactions for the synthesis of 1-benzyl-2,5-dimethyl pyrrole (**3h**) and 1-phenyl-2,5-dimethyl pyrrole (**3a**) carried out with $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ require shorter reaction times and give higher yields.

Conclusion

In summary, a new, simple catalytic protocol to synthesize *N*-substituted pyrroles by condensation of amines or diamine with 2,5-hexanedione using $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ under solvent-free conditions at room temperature has been developed. The short reaction times, simple experimental procedure and product isolation, wide applicability, good to excellent yields, mild reaction conditions, and use of nontoxic, noncorrosive, inexpensive and readily available Lewis acid catalyst are important features of this new method. Recovery and reuse of catalyst is also satisfactory,



Scheme 3.

Table 4. Comparison of some other procedures with the present method for the synthesis of **3h** and **3a** from **1h**, **1a** and **2a**

Entry	Catalyst (loading)	Media	Time	Product/yield ^a (%)	Reference
1	I ₂ (0.1 mmol, 0.025 g)	THF, r.t.	9 h	3h (89)	[20]
2	Bi(NO ₃) ₃ ·5H ₂ O (1 mmol)	CH ₂ Cl ₂ , r.t.	10 h	3h (95)	[24]
3	Sc(OTf) ₃	Solvent-free, 30 °C	30 min	3h (94)	[23]
4	InBr ₃ (5 mol%)	CH ₂ Cl ₂	1 h	3h (84)	[26]
5	In(OTf) ₃ (5 mol%)	CH ₂ Cl ₂	0.5 h	3h (90)	[26]
6	Microwave	Ether	0.5 h	3h (90)	[31]
7	<i>p</i> -TSA	C ₆ H ₆ /80 °C	1h	3h (84)	[18b]
8	Montmorillonite, KSF (1 g)	CH ₂ Cl ₂ , r.t.	10 h	3h (95)	[20]
9	α-Zr(KPO ₄) ₂	Solvent-free	2 h	3h (78)	[47]
10	ZrOCl ₂ ·8H ₂ O (2.5 mol%)	Solvent-free, r.t.	5 min	3h (97)	Table 2
11	ZrOCl ₂ ·8H ₂ O (2.5 mol%)	Solvent-free, r.t.	15 min	3a (93)	Table 2
12	Cu(OTf) ₂ (5 mol%)	Solvent-free, r.t.	30 min	3a (78)	[23]
13	Bi(OTf) ₃ (5 mol%)	Solvent-free, r.t.	25 min	3a (72)	[23]
14	CuCl ₂ (40 mol%)	Solvent-free, r.t.	25 min	3a (34)	[23]
15	Bi(NO ₃) ₃ ·5H ₂ O (1 mmol)	CH ₂ Cl ₂ , r.t.	600 min	3a (96)	[24]
16	Cationic exchange resin (Dowex 50 w, 1.63 g)	H ₂ O/130 °C	5 h	3a (85)	[48]

^a Isolated yields. r.t., Room temperature.

which demonstrates the cost efficiency and green aspect of our methodology.

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