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Catalytic applications of nano β-PbO in Paal–Knorr reaction

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Abstract

Several 2,5-dimethyl-*N*-substituted pyrroles were prepared by the condensation of different substituted anilines with 2,5-hexanedione using nano lead oxide as an efficient and recyclable catalyst. All the synthesized compounds are confirmed through IR, ^{1}H NMR, ^{13}C NMR and mass spectral data. Nano lead oxide β-PbO (P85) was prepared by dissolving lead acetate dihydrate in 1-propanol at a pH 9.0 under stirring at 85 °C. The structural study and surface morphology of the lead oxide (PbO) were characterized using X-ray diffraction (XRD), Scanning electron microscopy (SEM) and the functional groups of the PbO sample were investigated using infrared spectrophotometer.

Keywords: 2,5-Dimethyl-*N*-substituted pyrroles; Nano β-PbO; Spectral data; Catalyst characterization

Among the various classes of heterocyclic compounds, pyrroles have broad synthetic utility in medicine, materials science and organic synthesis [1]. Consequently, the enormous number of procedures has been developed for the construction of pyrroles. The classic methods for pyrrole synthesis are as follows: (i) the Hantzsch reaction [2], (ii) the Knorr reaction [3], (iii) the Paal–Knorr reaction [4] and (iv) some other methods were also reported [5]. The Paal–Knorr reaction, one of the most common approaches in which γ-diketone is converted to pyrroles from the reaction with primary amines (or ammonia) in the presence of various promoting agents such as HCl, *p*-TSA, HOAc, H_2SO_4 [6], I_2, Al_2O_3, montmorillonite [7], different metal complexes [8] as catalysts. Additionally, the above cyclocondensation process could proceed in ionic liquid [9], microwave irradiation [10], or ultrasound irradiation using $ZrCl_4$ as catalyst [11]. However, there are some limitations with these methodologies such as prolonged reaction times, elevated temperatures, moisture sensitive/hazardous catalysts, use of costly ionic liquids and use of an additional microwave oven or ultrasonic processor. Thus, the development of new catalysts with great efficiency, environmental friendly, convenient procedure, and delivery of better yield methods for the synthesis of pyrroles is of great interest.

Generally red colored lead oxide is called as litharge. This litharge is used primarily in the manufacture of various ceramic products. Moreover, lead oxide has important applications in the production of many lead chemicals, dry colors, soaps (*i.e.*, lead stearate), and driers for paint. Lead oxide (PbO) has been used as a catalyst, with excellent results, in one pot synthesis of quinoxalines [12]. Along this line, we found that lead oxide is an effective catalyst for the one pot synthesis of substituted pyrroles by using Paal–Knorr reaction. Herein, we report a simple and efficient

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method for the preparation of substituted pyrroles *via* condensation of γ-diketone and different substituted primary amines using nano level lead oxide as a catalyst and also the synthesis, characterization of PbO was discussed.

1. Results and discussion

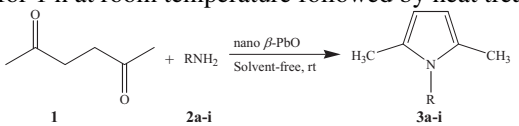
The *N*-substituted 2,5-dimethylpyrroles (**3a–i**) were prepared according to the synthetic pathway described in Scheme 1. γ-Diketone compound 2,5-hexanedione (**1**) was treated with different substituted primary amines (**2a–i**) in the presence of catalytic amount of nano level lead oxide under solvent free conditions to produce the corresponding *N*-subsituted-2,5-dimethylpyrroles. The nano level lead oxide catalyzed synthesis of *N*-sustituted-2,5-dimethylpyrroles (**3a–i**) was monitored by thin layer chromatography. The crude products were purified by recrystallization with 10% aqueous methanol led to the substituted pyrroles (**3a–i**) in moderate to good yields. The structures of known compounds were confirmed mainly based on their melting points, IR, ^{1}H NMR spectral data and structures of unknown compounds were confirmed by IR, ^{1}H NMR, ^{13}C NMR and mass spectral data.

In order to evaluate the catalytic efficiency of nano *β*-PbO and to determine the most appropriate reaction conditions; initially a model study was carried out on the synthesis of 2,5-dimethyl-*N*-phenylpyrrole (**3a**) by the condensation of 2,5-hexandione and aniline in different sets of reaction conditions (Table 1). Among the tested solvents such as acetonitrile, ethanol, methanol and solvent free conditions using various catalyst ratios, the condensation of acetonyl acetone and aniline was best catalyzed by 20 mol% of nano *β*-PbO in solvent free conditions under stirring at room temperature; it is also found to be novel, one-pot combination and exclusively gave 2,5-dimethyl-*N*-phenylpyrrole (**3a**) in 92% in 60 min (Table 1, entry 3). The recyclability of nano PbO was also investigated, and it could be recycled three times without distinct loss of activity (Table 1, entry 3). Particularly, we became aware of another useful role of PbO catalyst, that is, the coordinative activation of carbonyl functions of the 2,5-hexandione, which is trapped by different substituted amines to give the product in good yields. To extend the scope of this reaction, we applied the optimal protocol to a variety of amines and the results are summarized in Table 2. In all cases, nano *β*-PbO catalyzed Paal–Knorr condensation reaction proceeded smoothly and gave the corresponding products in good yield. Nano *β*-PbO was prepared by dissolving lead acetate dihydrate in 1-propanol at a pH 9.0, the solution was continuously stirred for 1 h at room temperature and then stirred at 85 °C for 12 h. The structural study, surface morphology and functional groups of the *β*-PbO were characterized by using X-ray diffraction pattern (Fig. 1), SEM (Fig. 2) and infrared spectrophotometer (Fig. 3), respectively.

2. Experimental

2.1. Typical procedure for the synthesis of nano β-PbO

Four grams of lead acetate dihydrate was dissolved in 150 mL of 1-propanol and pH is maintained at 9.0. The solution was continuously stirred for 1 h at room temperature followed by heat treatment and the precursor solutions



Scheme 1. Synthesis of 2,5-dimethyl-*N*-substitutedpyrroles catalyzed by nano *β*-PbO.

Table 1
Paal–Knorr reaction of acetonylacetone (**1**) and aniline (**2a**) under different reaction conditions.

Entry	Solvent	Catalyst loading (mol%)	Temperature (°C)	Time (min)	Yield[a] (%)
1	Solvent free	0	RT	300	20
2	Solvent free	10	RT	120	78
3	Solvent free	20	RT	60	92, 90, 87[b]
4	Acetonitrile	20	RT	120	63
6	Ethanol	20	RT	120	81
7	Methanol	20	RT	60	90
8	Methanol	Excess	RT	60	89

RT = room temperature.
[a] Isolated yields.
[b] Catalyst was reused for three times.