



Preliminary communication/Communication

Organotin–oxotungstate coordination polymer: An efficient catalyst for the selective oxidation of amines

This article is dedicated to Professor Firouz Matloubi Moghaddam.

Fatemeh Nikbakht, Akbar Heydari*

Chemistry Department, Tarbiat Modares University, P. O. Box 14155-4838 Tehran, Iran

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ABSTRACT

The organometallic coordination polymer $[(n\text{Bu}_3\text{Sn})_2\text{WO}_4]$ catalyzed the selective oxidation of secondary and primary amines to nitrones and oximes, respectively. The catalyst was found to be reusable for five catalytic cycles without any appreciable loss in activity. Under the optimized reaction conditions [4 mol% catalyst, 3–4 equiv of hydrogen peroxide (30 wt%, aqueous solution), methanol as the solvent, r.t.], the corresponding nitrones and oximes were obtained with good efficiency.

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1. Introduction

Coordination polymers have recently attracted much research attention due to their potential application in areas of synthetic chemistry, materials science and catalysis [1]. Coordination polymers are solid phase catalysts and as such, can easily be separated from the reaction mixtures and reused without any further treatment. We have recently been interested in the study of coordination polymers and potential catalytic activity of these compounds. The research has demonstrated that the silver (I)-based coordination polymer $[\text{Ag}(\mu\text{-bpfb})(\text{N}_3)]_n$ is able to catalyze the oxidation of amines into hydroxylamines using urea hydrogen peroxide [2]. Studies on tungsten coordination polymers are rare and very little work has been reported on the catalytic activity of these compounds in oxidation reactions. A perusal of the related

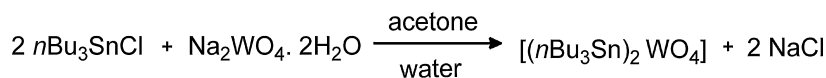
literature demonstrated that a number of methods have been developed for the oxidative coupling of the primary amines and oxidation of the secondary amines into imines using metal–organic frameworks (MOFs) and coordination polymers as the solid phase catalysts [3,4]. However, no precedent has yet been reported for the oxidative syntheses of nitrones and oximes from amines using coordination polymers as the catalyst, apart from the work reported by Abrantes et al. [5].

In this study, the investigation illustrated the efficient catalytic oxidation of secondary amines to nitrones using hydrogen peroxide as the primary oxidant in the presence of the organometallic coordination polymer $[(n\text{Bu}_3\text{Sn})_2\text{WO}_4]$. Furthermore, this investigation examined the catalytic activity of this compound in the oxidation of the primary amines. Hydrogen peroxide was used as the stoichiometric oxidant because, it is non-toxic and water is produced as the only by-product; as a result, it is considered as environmentally safe.

There are a large number of related articles published on the synthesis of azomethine *N*-oxides, which are commonly

* Corresponding author.

E-mail addresses: f.nikbakht@modares.ac.ir, fanikbakht@gmail.com (F. Nikbakht), heydar_a@modares.ac.ir (A. Heydari).



Scheme 1. Preparation of $[(n\text{Bu}_3\text{Sn})_2\text{WO}_4]$ coordination polymer.

Table 1
Optimization of the reaction conditions^a.

Entry	Oxidant	Catalyst (mol%)	Time (h)	Yield (%) ^b
1	H ₂ O ₂	No catalyst	24	Trace
2	H ₂ O ₂	3	12	70
3	H ₂ O ₂	4	5	85
4	H ₂ O ₂	5	5	85
5	TBHP	4	12	n.r.
6	NaOCl	4	12	n.r.

TBHP: *tert*-butylhydroperoxide; n.r.: no reaction. r.t.: room temperature. equiv.: equivalent.

^a Reaction conditions: dibenzylamine (1 mmol), catalyst, oxidant (3–4 equiv), CH₃OH (2 mL), r.t.

^b Isolated yield of *N*-benzylidenebenzylamine *N*-oxide.

known as nitrones. Nitrones are important because, they are relatively stable as compared to analogous azomethine imines [6] and are key synthetic intermediates. Nitrones are the building blocks in the synthesis of various bioactive compounds. α -Aryl-*N*-alkyl nitrones, have been recognized as potential agents for treating strokes, for example *tert*-butylbenzyl nitrone (PBN) acts as a radical spin trapping agent and exhibits antioxidant and neuroprotective activity against oxidative damage [7]. Several methods are available for the synthesis of nitrones. Selective catalytic oxidation of secondary amines has long been recognized as an atom efficient method for producing nitrones; which occurs with a variety of oxidizing agents and catalysts [8–10].

Organotin–oxotungstate coordination polymer $[(n\text{Bu}_3\text{Sn})_2\text{WO}_4]$, has been prepared by Abrantes group [11] and applied as an efficient catalyst for the epoxidation of olefins by hydrogen peroxide, selective oxidation of aniline derivatives to nitroso compounds [12], and for the oxyfunctionalization of monoterpenes [13]. In this present work, the investigation was focused on further examination of the catalytic potential of this compound in the oxidation of primary and secondary amines using aqueous hydrogen peroxide.

2. Results and discussion

The organometallic coordination polymer $[(n\text{Bu}_3\text{Sn})_2\text{WO}_4]$ was prepared according to a reported procedure [11], as

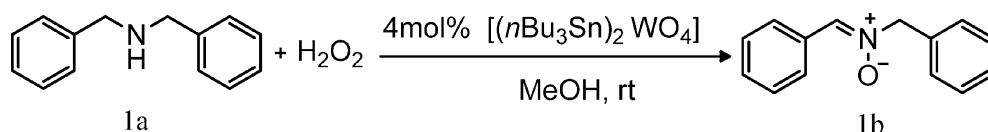
shown on Scheme 1. It was synthesized from commercially available sodium tungstate and tri (*n*-butyl) tin chloride in 92% yield. The FT-IR spectra and the XRD diffraction patterns of the resulting white powder were the same as those reported in other studies and these observations confirm synthesis of $[(n\text{Bu}_3\text{Sn})_2\text{WO}_4]$ [11,12].

To determine the optimal conditions for the oxidation of amines, various loadings of coordination polymer $[(n\text{Bu}_3\text{Sn})_2\text{WO}_4]$ were initially tested as a catalyst or catalyst precursor for the oxidation of dibenzylamine at room temperature, using hydrogen peroxide (30 wt%, aqueous solution) as the stoichiometric oxidant with methanol as the solvent (Table 1). The absence of catalyst resulted in a non-selective oxidation of dibenzylamine (Table 1, entry 1). The optimum condition for the selective oxidation of **1a** into the corresponding nitronone, **1b** required the use of at least 4 mol% of the coordination polymer, $[(n\text{Bu}_3\text{Sn})_2\text{WO}_4]$ (Table 1, entry 3). The oxidation of dibenzylamine in the presence of 4 mol% $[(n\text{Bu}_3\text{Sn})_2\text{WO}_4]$, using other oxidants like *tert*-butylhydroperoxide (TBHP) and sodium hypochlorite (NaOCl) was unsuccessful (Table 1, entry 5–6), therefore hydrogen peroxide was selected as the optimal efficient oxidant.

In the optimum conditions, oxidation of dibenzylamine by hydrogen peroxide proceeded in 5 hours at room temperature in the presence of 4 mol% of the catalyst ($[(n\text{Bu}_3\text{Sn})_2\text{WO}_4]$), to give *N*-benzylidenebenzylamine *N*-oxide, in 85% yield (Table 1, entry 3). Turnover number of the catalyst was approximately 21 (Scheme 2).

The catalytic activity of coordination polymer ($[(n\text{Bu}_3\text{Sn})_2\text{WO}_4]$), was evaluated in the oxidation of various secondary amines with aqueous hydrogen peroxide (30 wt%), in methanol, at room temperature. Results are presented in Table 2. Benzylic and symmetrical secondary amines such as dibenzylamine (**1a**), di (4-methylbenzyl)amine (**2a**), di (2-methoxybenzyl)amine (**3a**) were readily converted into their corresponding nitrones, as anticipated (Table 2, entries 1–3).

The oxidation processes of unsymmetrical benzylic amines such as *N*-*tert*-butylbenzylamine (**4a**), *N*-*n*-butylbenzylamine (**5a**), *N*-*iso*-propylbenzylamine (**6a**), and *N*-cyclohexylbenzylamine (**7a**) were tested. The nature of the alkyl group demonstrated no significant affect on the nitronone yield, however, those hindered amines reacted slightly slower than did the others (Table 2, entries 4–7). *Tert*-butylbenzylamine (**4a**) have no alpha protons on one



Scheme 2. Oxidation of dibenzylamine using (30 wt% aqueous solution) promoted by $[(n\text{Bu}_3\text{Sn})_2\text{WO}_4]$.

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