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PII:	S0040-4039(13)01655-9
DOI:	http://dx.doi.org/10.1016/j.tetlet.2013.09.090
Reference:	TETL 43590
To appear in:	Tetrahedron Letters
Received Date:	22 May 2013
Revised Date:	2 September 2013
Accepted Date:	20 September 2013



Please cite this article as: Nikbakht, F., Heydari, A., Saberi, D., Azizi, K., Oxidation of secondary amines to nitrones using magnetically separable tungstophosphoric acid supported on silica-encapsulated  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles, *Tetrahedron Letters* (2013), doi: http://dx.doi.org/10.1016/j.tetlet.2013.09.090

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# Oxidation of secondary amines to nitrones using magnetically separable tungstophosphoric acid supported on silica-encapsulated $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles

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#### ARTICLE INFO

### ABSTRACT

Article history: Received Received in revised form Accepted Available online

Keywords: Oxidation Secondary amines Nitrones Tungstophosphoric acid Magnetic separation Superparamagnetic tungstophosphoric acid supported on silica-encapsulated  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> was used as an efficient catalyst for the direct oxidation of secondary amines to nitrones with hydrogen peroxide as the oxidant. The catalyst could be recycled up to four times without significant loss of activity.

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Oxidative transformations of amines offer potentially interesting new routes to important chemical building blocks.<sup>1</sup> Selective catalytic oxidation of secondary amines to nitrones,<sup>2</sup> imines<sup>3</sup> and hydroxylamines<sup>4</sup> have been explored. Nitrones have long been regarded as useful intermediates for the synthesis of heterocyclic compounds.<sup>5</sup> Moreover, they have relevant application as spin traps<sup>6</sup> and therapeutics in age-related diseases.<sup>7</sup> Conventional strategies for the synthesis of these compounds include condensation of carbonyl compounds with monosubstituted hydroxylamines,<sup>8</sup> N-alkylation of oximes<sup>9</sup> and oxidation of hydroxylamines,<sup>10</sup> imines<sup>11</sup> and secondary amines.<sup>2</sup> Among these methods, selective oxidation of imines and secondary amines to nitrones is the most attractive because amines are readily accessible compared to hydroxylamines. Oxidation of secondary amines to nitrones has been performed with various types of peroxides as the oxidant: hydrogen peroxide, urea-hydrogen peroxide and alkyl hydroperoxide in the presence of various catalysts such as Ti(IV),<sup>2k</sup> W(VI),<sup>2p,2s</sup> Mo(VI),<sup>2r</sup> Pt(II),<sup>2m</sup> and  $CH_3ReO_3$ .<sup>13,2u</sup> Excellent yields have been obtained for the catalytic oxidation of certain amines. However, in some cases, there are disadvantages such as low selectivity.<sup>2h-i</sup> problems with catalyst recovery and procedures that demand harsh conditions. In addition, with highly reactive nitrones, overoxidation and hydrolysis can be significant problems.<sup>2d,12</sup> Consequently, it is desirable to use a cheap and environmentally benign oxidant in combination with suitable catalysts in order to overcome these problems.

Previously, we reported the preparation of a novel version of solid tungstophosphoric acid supported on silica-encapsulated  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> ( $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>@SiO<sub>2</sub>-H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>)<sup>14</sup> as a magnetic, recoverable catalyst. Metal complexes of tungsten and molybdenum, are active catalysts for the oxidation of secondary amines to nitrones.<sup>2d,r</sup> Hence it was decided to investigate the catalytic activity of this magnetic compound for the oxidation of amines. Moreover, among the various peroxides, aqueous hydrogen peroxide was chosen as the most suitable oxidant as it is cheap, environmentally safe and easy to handle. Facile separation of the catalyst (up to four times) and selectivity are other important benefits of this system.

In an initial study, dibenzylamine was used as a model substrate to optimize the conditions for the oxidation of secondary amines to nitrones. Oxidation of this substrate in methanol as the solvent at room temperature, in the absence of a catalyst, was tested and formation of a small amount of the desired product showed that the presence of a catalyst was necessary for this reaction (Table 1, entry 1). Adding silicaencapsulated  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles as the catalyst had little impact on the progress of the reaction (Table 1, entry 2). In contrast, addition of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>@SiO<sub>2</sub>-H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> [10 mg, 1.1 mol% (determined by back titration)] as the catalyst enabled the oxidation to give the corresponding nitrone, (Z)-Nbenzylidenebenzylamine N-oxide in 85% yield (Table 1, entry 4). Next, we examined the effects of parameters such as the amount of catalyst, temperature and solvent. Screening organic solvents (MeOH, CH<sub>3</sub>CN, CH<sub>2</sub>Cl<sub>2</sub>, DMSO) as well as water, showed that the best yield was obtained in MeOH (Table 1, entries 3-8).

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Raising the reaction temperature had a negative effect on the yield (Table 1, entry 5). Increasing the amount of catalyst gave no change in the reaction rate, but decreasing the amount of catalyst prolonged the reaction time. All the reactions were carried out under an argon atmosphere (reaction under atmospheric pressure gave a mixture of products). Therefore, the optimum conditions for this reaction are as follows: 1.1 mol% of catalyst, MeOH as the solvent, room temperature, argon atmosphere.<sup>15</sup>

#### Table 1

Optimization of the reaction conditions using the model system.<sup>a</sup>

Entry	Catalyst (mol%)	Solvent	Temp.	p. Time (h)	
			(°C)	/Yield (%) <sup>b</sup>	
1	No catalyst	MeOH	23	24/trace	
2	$\gamma$ -Fe <sub>2</sub> O <sub>3</sub> @SiO <sub>2</sub> (1.1)	MeOH	23	24/10	
3	$\gamma$ -Fe <sub>2</sub> O <sub>3</sub> @SiO <sub>2</sub> - PW <sup>c</sup> (1.1)	$H_2O$	23	2/70 <sup>d</sup>	
4	$\gamma$ -Fe <sub>2</sub> O <sub>3</sub> @SiO <sub>2</sub> - PW (1.1)	МеОН	23	2/85	
5	$\gamma$ -Fe <sub>2</sub> O <sub>3</sub> @SiO <sub>2</sub> - PW (1.1)	MeOH	60	24/40	
6	γ-Fe <sub>2</sub> O <sub>3</sub> @SiO <sub>2</sub> - PW (1.1)	DMSO	23	24/10	
7	γ-Fe <sub>2</sub> O <sub>3</sub> @SiO <sub>2</sub> - PW (1.1)	CH <sub>3</sub> CN	23	24/50 <sup>d</sup>	
8	γ-Fe <sub>2</sub> O <sub>3</sub> @SiO <sub>2</sub> - PW (1.1)	$CH_2Cl_2$	23	48/0	
9	γ-Fe <sub>2</sub> O <sub>3</sub> @SiO <sub>2</sub> - PW (2.2)	MeOH	23	2/85	
10	γ-Fe <sub>2</sub> O <sub>3</sub> @SiO <sub>2</sub> - PW (0.55)	MeOH	23	24/85	

 $^{\rm a}$  Reaction conditions: dibenzy lamine (1 mmol),  $\rm H_2O_2$  (3 equiv.), solvent (2 mL), Ar atm.

<sup>b</sup> Isolated yield

<sup>c</sup>γ-Fe<sub>2</sub>O<sub>3</sub>@SiO<sub>2</sub>-H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>

<sup>d</sup> Benzaldehyde was formed as a by-product

Under these conditions, a variety of secondary amines were used as substrates for the synthesis of the corresponding nitrones (Scheme 1). As can be seen in Table 2, various nitrones were synthesized in moderate to good yields. All the products are known compounds (except **2b** and **2c**)<sup>16</sup> and were characterized by comparison of their IR, <sup>1</sup>H NMR and <sup>13</sup>C NMR spectroscopic data and respective melting points with reported values.<sup>24, 8f, 17</sup>



Scheme 1. Synthesis of nitrone derivatives in the presence of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>@SiO<sub>2</sub>-H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> as the catalyst.

Generally speaking, the presence of an electron-releasing group such as methyl or methoxy on the benzyl moiety increased the product yield (Table 2, entries 2 and 3). *N*-Benzyl-*tert*-butylamine was converted into the corresponding nitrone in good yield (Table 2, entry 4). Oxidation of less activated dibutylamine was investigated and the related nitrone was obtained in a good yield, but required more time compared to benzyl derivatives (Table 2, entry 5). In the case of unsymmetrical amines, there is the possibility of forming two products, but using these reaction conditions, only the thermodynamically more stable product was formed (Table 2, entries 6-8).

The reusability of the catalyst was examined in the synthesis of compound **2a**. When the reaction was complete, the catalyst was adsorbed on to the side-wall of the reaction vessel with the aid of an external magnet. The catalyst was washed with methanol three times and each time the catalyst separated easily from the solution by attaching an external magnet onto the reaction vessel, followed by decanting the solution. The remaining catalyst was dried in a vacuum and reused in a subsequent reaction. More than 95% of the catalyst could usually be recovered from each reaction. The catalyst could be reused in four runs without significant loss of its catalytic activity (see entry 1, Table 2).

Mechanistic investigations on tungsten-based oxidation systems with hydrogen peroxide have shown that  $[PO_4\{WO(O_2)_2\}_4]^{3-}$  is a catalytically important species generated by the reaction of  $H_3PW_{12}O_{40}$  with excess hydrogen peroxide, and is the active complex for the oxidation of variety of organic compounds.18 Tomaseli and co-workers reported that the oxidation of secondary amines by anionic mononuclear Mo(VI) and W(VI) peroxo complexes, involves a rate determining nucleophilic attack of the amine onto a peroxide oxygen with formation of the corresponding hydroxylamine, followed by a faster step in which the hydroxylamine is oxidized to a nitrone.<sup>19</sup> In order to confirm the above-mentioned mechanism in the presence of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>@SiO<sub>2</sub>-H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> nanoparticles, oxidation of N,N-dibenzylhydroxylamine was performed under the optimized reaction conditions and (Z)-N-benzylidenebenzylamine N-oxide was formed almost immediately. This observation seems to support the possibility that the hydroxylamine may represent the first intermediate generated by nucleophilic attack of the amine on the peroxide oxygen. This intermediate is then converted into the nitrone in a much faster subsequent step (Scheme 2). It has to be pointed out that when an imine was exposed to the oxidation conditions, only degradation products were obtained. This result eliminates the hypothesis of an imine as intermediate in the reaction mechanism.



Scheme 2. Proposed mechanism for the  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>@SiO<sub>2</sub>-H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>-catalyzed oxidation of secondary amines to nitrones.

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#### Table 2

Catalytic oxidation of secondary amines by hydrogen peroxide in the presence of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>@SiO<sub>2</sub>-H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> nanoparticles as the catalyst.<sup>a</sup>

Entry	Substrate	Product	Time (h)	Yield (%) <sup>b</sup>	TON <sup>c</sup>	$TOF(h^{-1})^d$	Ref.
1		N O 2a	2	85 (85, 83, 80) <sup>e</sup>	77.2	38.6	8f
2		N O- 2b	2	90	81.8	40.9	-
3	OMe OMe	OMe OMe	1	87	79.1	79.1	-
4		N O- 2d	4	85	77.2	19.3	17
5	N H 1e	N = N = N = N = N = N = N = N = N = N =	12	70	63.6	5.3	2d
6	OMe N OMe H O If	OMe , O O 2f	12	65	58.8	4.9	2d
7	N Ig	N O- 2g	3	53	48.3	16.1	8f
8		N 0- 2h	3.5	55	49.7	14.2	17

<sup>a</sup> Reaction conditions: amine (1 mmol), H<sub>2</sub>O<sub>2</sub> (3 equiv.), CH<sub>3</sub>OH (2 mL), r.t., Ar atm.

<sup>b</sup> Isolated yield.

<sup>c</sup> Turnover number (average number of product molecules produced per mole of the catalyst).

<sup>d</sup> Turnover frequency (turnover number per hour).

<sup>e</sup> The reaction was accomplished with recycled catalyst.

In summary, this report describes an efficient method for the selective oxidation of secondary amines to nitrones. The  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>@SiO<sub>2</sub>-H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> nanoparticles can be easily separated from the products and can be reused. The reactions were complete after 1-12 hours producing good yields of the nitrones, which were comparable with yields obtained by known methods.

#### Acknowledgments

We are thankful to Tarbiat Modares University for financial support of this work.

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- 2012, 1027, 156–161.15. General procedure for the synthesis of nitrone derivatives: The
- 13. General procedure for the synthesis of infrone derivatives. The secondary amine (1 mmol) was added to a mixture of catalyst (0.01 g, 1.1 mol%) and methanol (2 mL). The mixture was stirred for 5 min, under an argon atmosphere, and then H<sub>2</sub>O<sub>2</sub> (3 equiv.) was added in two or three portions. The mixture was stirred at room temperature until completion of the reaction [monitored by TLC (CH<sub>2</sub>Cl<sub>2</sub>/MeOH, 95:5)]. After complete disappearance of the amine, the catalyst was separated from the reaction mixture using an external magnet, washed with MeOH three times to remove all residual products, and then dried for reuse in a subsequent run. Evaporation of the solvent gave the crude product, which was purified by recrystallization (CH<sub>2</sub>Cl<sub>2</sub>/n-hexane) or by preparative thin-layer chromatography. All isolated products gave satisfactory physical and spectral data (melting points, FT-IR, <sup>1</sup>H NMR and <sup>13</sup>C NMR) compared with those reported in the literature.
- 16. The spectroscopic data of nitrones 2b and 2c are reported since no literature data are available.
  4-Methylbenzylidene-4-methylbenzylamine N-oxide (2b) (entry 2, Table 2): White crystals, 90% yield, Mp 121-122 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ= 8.02-8.04 (m, 2H, ArH ortho to -CH=N(O)), 7.11-7.29 (m, 7H, ArH and -CH=N(O)), 4.92 (s, 2H, CH<sub>2</sub>), 2.29 (s, 6H, 2CH<sub>3</sub>); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ= 140.8, 138.9, 138.8, 134.2, 134.1, 130.3, 129.8, 129.7, 129.6, 129.3,

129.1, 128.7, 127.8, 70.8, 21.7, 21.2; FT-IR (KBr): 3069(w), 3020(m), 2919(m), 1588(w), 1511(w), 1457(s), 1418(m), 1351(w), 1224(w), 1162(vs), 1117(w), 949(m), 860(m), 804(s) cm<sup>-1</sup>; MS m/z: 239.2 (M<sup>+</sup>).

2-Methoxybenzylidene-2-methoxybenzylamine *N*-oxide (**2c**) (entry 3, Table 2): White crystals, 87% yield, Mp 108-109  $^{0}$ C;  $^{1}$ H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$ =7.88 (s, 1H, -CH=N(O)), 6.77-7.26(m, 8H, ArH), 5.03 (s, 2H, CH<sub>2</sub>), 3.78 (s, 3H, OCH<sub>3</sub>), 3.75(s, 3H, OCH<sub>3</sub>);  $^{13}$ C NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$ = 157.7, 156.9, 131.4, 131.3, 130.2, 128.8, 122.0, 120.8, 120.7, 120.5, 119.8, 110.6, 109.7, 66.3, 55.5, 55.4; FT-IR (KBr): 3150 (w), 2935 (w), 1603(m), 1465(s), 1297(w), 1246(s), 1141(w), 1023(m), 806(w), 750(s) cm<sup>-1</sup>; MS *m/z*: 271.1 (M<sup>+</sup>).

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