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PII: S0040-4039(17)30012-6  
DOI: <http://dx.doi.org/10.1016/j.tetlet.2017.01.012>  
Reference: TETL 48515

To appear in: *Tetrahedron Letters*

Received Date: 10 December 2016  
Revised Date: 2 January 2017  
Accepted Date: 3 January 2017

Please cite this article as: Ma, J., Hong, C., Wan, Y., Li, M., Hu, X., Mo, W., Hu, B., Sun, N., Jin, L., Shen, Z.,  
Aerobic oxidation of secondary alcohols in water with ABNO/*tert*-butyl nitrite/KPF<sub>6</sub> catalytic system, *Tetrahedron  
Letters* (2017), doi: <http://dx.doi.org/10.1016/j.tetlet.2017.01.012>

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**Aerobic oxidation of secondary alcohols in water with ABNO/*tert*-butyl  
nitrite/KPF<sub>6</sub> catalytic system**

Jiaqi Ma, Chao Hong, Yan Wan, Meichao Li, Xinquan Hu, Weimin Mo, Baoxiang Hu, Nan Sun,

Liqun Jin, Zhenlu Shen\*

*College of Chemical Engineering, Zhejiang University of Technology, Hangzhou 310014, China*

*E-mail address: zhenlushen@zjut.edu.cn*

*Tel.: +86-571-88320416, fax: +86-571-88320103*

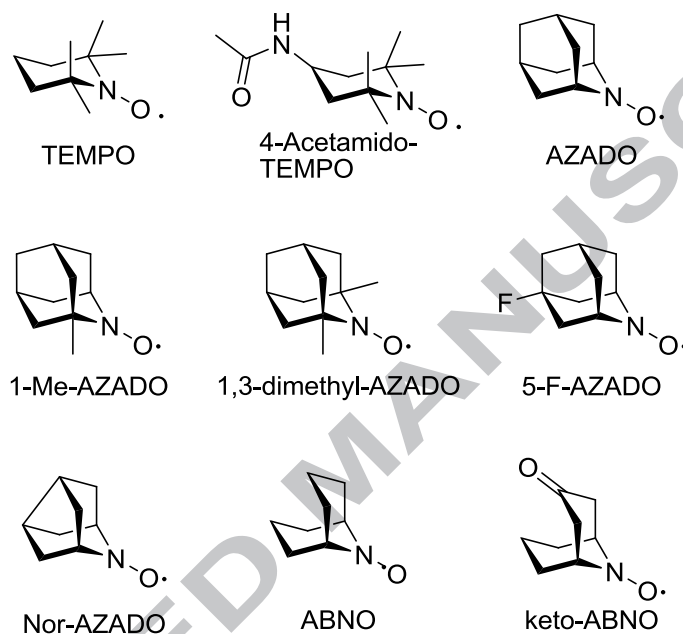
**ABSTRACT:**

A green and efficient transition-metal free ABNO/*tert*-butyl nitrite/KPF<sub>6</sub>-catalyzed aerobic oxidation of secondary alcohols in water has been achieved. Under the optimal reaction conditions, a number of secondary aliphatic alcohols and secondary benzylic alcohols can be converted to their corresponding ketones in excellent yields (up to 99%).

**Keywords:** Oxidation; ABNO; Secondary alcohols; Oxygen; Water

The oxidation of primary and secondary alcohols to their corresponding carbonyl compounds is one of the most fundamental reactions in organic synthesis.<sup>1</sup> Traditionally, various kinds of classical oxidation methods with stoichiometric oxidants were adopted, including Corey Oxidation with pyridinium chlorochromate(PCC),<sup>2</sup> Dess-Martin Oxidation with periodinane(DMP),<sup>3</sup> Ley's Oxidation,<sup>4</sup> Swern Oxidation<sup>5</sup> and so on. However, these reactions generate or use toxic reagents which would cause serious environmental problems. Molecular oxygen has attracted great attention due to its remarkable advantages, such as abundant, inexpensive and clean. There is no doubt that molecular oxygen as oxidant for alcohol oxidation was the best alternative from both economical and environmental considerations.<sup>6</sup> Stable nitroxyl radicals 2,2,6,6-tetramethylpiperidine-1-oxyl(TEMPO) and its derivatives have been widely used to catalyze the oxidation of alcohols. Many of the highly efficient TEMPO/transition-metal catalytic systems have been developed for aerobic alcohol oxidation.<sup>7</sup> However, toxic or expensive metal catalysts are still involved in these systems. Previously, we have reported several transition-metal free aerobic alcohol oxidation systems, such as TEMPO/Br<sub>2</sub>/NaNO<sub>2</sub>/O<sub>2</sub>,<sup>8</sup> TEMPO/1,3-dibromo-5,5-dimethylhydantoin/NaNO<sub>2</sub>/O<sub>2</sub>,<sup>9</sup> TEMPO/HBr/*tert*-butyl nitrite (TBN) /O<sub>2</sub>,<sup>10</sup> TEMPO/TBN/O<sub>2</sub><sup>11</sup> and TEMPO/DDQ/TBN/O<sub>2</sub>.<sup>12</sup> Recent years, several types of less structurally hindered bicyclic nitroxyls such as 2-azaadamantan-N-oxyl (AZADO), 1-Me-AZADO, 1,3-dimethyl-AZADO, 5-F-AZADO, and Nor-AZADO were reported by Iwabuchi and co-workers.<sup>13</sup> AZADO and its derivatives are more active alternatives to TEMPO for the efficient catalytic oxidation of various alcohols, especially structurally hindered secondary alcohols. However, these AZADO types of bicyclic nitroxyls are difficult to be synthesized. Compared with

AZADOs, 9-azabicyclo[3.3.1]nonan-N-oxyl (ABNO) was reported to have the similar activity (Scheme 1). Moreover, the synthetic route of ABNO is much shorter and simpler than that of AZADOs. ABNO exhibits highly catalytic activity in the aerobic oxidation of alcohols combined with  $\text{NO}_x$ , Cu or Fe.<sup>14</sup>

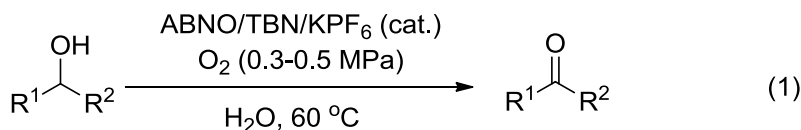


**Scheme 1.** Structures of different types of nitroxyl radicals

Water has been identified as a “green” and desirable solvent because it is benign to the environment.<sup>15</sup> The choice of water as a reaction medium is a charming research orientation. As a replacement for conventional organic solvents in chemical reactions, water is abundantly available, cheap, odorless, non-toxic and non-flammable. In addition to these advantages, ease of product isolation through simple phase separation, decantation or extraction is possible because most organic compounds are lipophilic. Catalytic oxidations of alcohols with nitroxyl radical/transition-metal in aqueous reaction media also have been studied.<sup>16</sup> Because of the limited solubility of reagents and the

activity of the catalysts, transition-metal free aerobic oxidation of alcohols with stable nitroxyl radicals in water is still uncommon. Previously, we reported a TEMPO/NaNO<sub>2</sub>/1,3-dibromo-5,5-dimethylhydantoin system,<sup>9</sup> which was suitable for the oxidation of benzylic alcohols in water, however, it was not efficient for aliphatic alcohols. Kakimoto *et al* developed a 1-Me-AZADO/NaNO<sub>2</sub>/HNO<sub>3</sub> system,<sup>17</sup> it could be simply applied to various benzylic alcohols under mild conditions, however, the obtain of 1-Me-AZADO needs a six-step synthesis from commercially available 1,3-adamantanediol. Zhang *et al* described an example of Cu/DMAP catalyst system,<sup>18</sup> which was applied in the aerobic oxidation of a variety of primary and secondary alcohols in water at room temperature, in the presence of TEMPO or ABNO. However, metal Cu was still involved. Overall, to develop a transition-metal free aerobic oxidation of alcohols with ABNO in water is still full of significance.

Herein, we report a new ABNO/TBN/KPF<sub>6</sub>/O<sub>2</sub> system for the aerobic oxidation of secondary alcohols in water (eq 1). Under the optimal reaction conditions, a variety of secondary aliphatic alcohols and benzylic alcohols can be converted to their corresponding ketones in good to excellent yields.

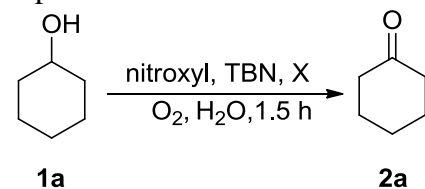


At the outset, cyclohexanol (**1a**) was selected as a model substrate to identify the optimal reaction conditions (Table 1). The oxidation of **1a** to cyclohexanone (**1b**) was carried out with 5 mol% ABNO, 5 mol% TBN in 10 mL water at 80 °C under 0.5 MPa of oxygen, it was found

that the conversion of **1a** was only 45% in 1.5 h (entry 1). When 5 mol% NaCl was added in the reaction system, the conversion of **1a** increased to 64%, this result showed that NaCl had played an important role in this reaction (entry 2). Other salts, including NaBF<sub>4</sub>, KBr and KPF<sub>6</sub> were also tested under the same reaction conditions (entries 3-5). We were delighted to find that the conversion of **1a** could be improved to 97% when KPF<sub>6</sub> was employed (entry 5). The effects of additives on the reaction might be relevant to the formal redox potential of oxoammonium salt/nitroxyl radical in the presence of different anions.<sup>19</sup> An investigation of the effect of nitroxyl radicals (entries 5-8) revealed that use of ABNO greatly increased the conversion of **1a**. The reactions with TEMPO, 4-acetamido-TEMPO and keto-ABNO did not proceed well, the conversion of **1a** was only 71%, 44% and 45%, respectively. Increasing the loading of ABNO from 5 mol% to 6 mol%, **1a** could be fully converted to **2a** (entry 9, >99%).

Encouraged by these results, the oxygen pressure and the reaction temperature were also tested. Entries 9-13 illustrate the impact of oxygen pressure and reaction temperature on the efficiency of this reaction. Reducing the oxygen pressure from 0.5 MPa to 0.4 MPa led to a lower conversion of **1a** (entries 9 and 10). To our delight, the reaction temperature of 70 °C and 60 °C were also suitable for the ideal transformation of **1a** (entries 11 and 12, >99%). Further decreasing the reaction temperature to 50 °C led to lower conversion of **1a** (entries 13, 68%). Thus 60 °C was chosen as the optimal reaction temperature. When the loading of TBN was reduced to 4 mol%, the conversion of **1a** went down to 80% accordingly (entry 14). In addition, reducing the loading of KPF<sub>6</sub> to 4 mol% could also obtain an excellent conversion of **1a** (entry

15, >99%). We wondered whether removing the water from reaction system, in other words, solvent-free system, would have the same or similar results, but the conversion of **1a** dropped into 14%, this low conversion suggested that water was important in the reaction. After detailed exploration of the reaction conditions with **1a** as the substrate, we chose 6 mol% ABNO, 5 mol% TBN and 4 mol% KPF<sub>6</sub> in 10 mL water at 60 °C under 0.5 MPa of O<sub>2</sub> as the optimal reaction conditions, **2a** could be obtained with 96% yield as determined by GC using an internal standard method in 1.5 h (entry 15).

**Table 1.**Optimization of the Reaction Conditions for Cyclohexanol Oxidation <sup>a</sup>

Entry	nitroxyl	Cat. (mol%)	TBN (mol%)	P(O <sub>2</sub> ) (MPa)	T <sup>b</sup> (°C)	X (mol%)	Conv. <sup>c</sup> (%)	Select. <sup>c</sup> (%)
1	ABNO	5	5	0.5	80	---	45	98
2	ABNO	5	5	0.5	80	NaCl(5)	64	99
3	ABNO	5	5	0.5	80	NaBF <sub>4</sub> (5)	74	98
4	ABNO	5	5	0.5	80	KBr(5)	69	99
5	ABNO	5	5	0.5	80	KPF <sub>6</sub> (5)	97	99
6	TEMPO	5	5	0.5	80	KPF <sub>6</sub> (5)	71	98
7	4-Acetamido- TEMPO	5	5	0.5	80	KPF <sub>6</sub> (5)	44	93
8	Keto-ABNO	5	5	0.5	80	KPF <sub>6</sub> (5)	45	96
9	ABNO	6	5	0.5	80	KPF <sub>6</sub> (5)	>99	99
10	ABNO	6	5	0.4	80	KPF <sub>6</sub> (5)	85	99

11	ABNO	6	5	0.5	70	KPF <sub>6</sub> (5)	>99	99
12	ABNO	6	5	0.5	60	KPF <sub>6</sub> (5)	>99	99
13	ABNO	6	5	0.5	50	KPF <sub>6</sub> (5)	68	98
14	ABNO	6	4	0.5	60	KPF <sub>6</sub> (5)	80.	99
<b>15</b>	<b>ABNO</b>	<b>6</b>	<b>5</b>	<b>0.5</b>	<b>60</b>	<b>KPF<sub>6</sub>(4)</b>	<b>&gt;99</b>	<b>99(96)<sup>d</sup></b>
16	ABNO	6	5	0.5	60	KPF <sub>6</sub> (3)	78	99
17 <sup>e</sup>	ABNO	6	5	0.5	60	KPF <sub>6</sub> (4)	14	93

<sup>a</sup> Reaction conditions: **1a** (30 mmol), H<sub>2</sub>O (10 mL).

<sup>b</sup> Oil bath temperature.

<sup>c</sup> Determined by GC with area normalization method.

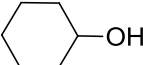
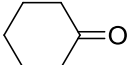
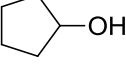
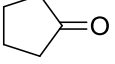
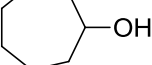
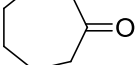
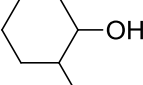
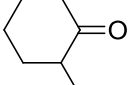
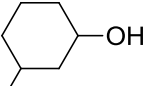
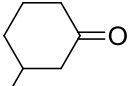
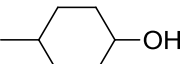

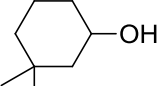
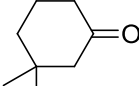
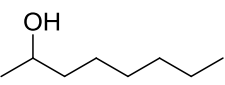
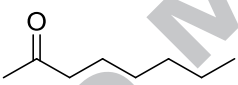
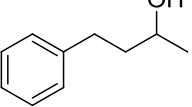
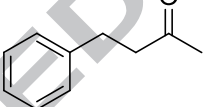
<sup>d</sup> Value in parenthesis was yield of **2a** determined by GC analysis using biphenyl as internal standard.

<sup>e</sup> H<sub>2</sub>O was not added.

Having gotten the optimal reaction conditions, a number of secondary aliphatic alcohols were examined firstly and the results are summarized in Table 2. Because of our initial efforts to acquire high conversion and selectivity of unactivated alcohol oxidation, cyclic alcohols, such as cyclopentanol (**1b**), cycloheptanol (**1c**) could be fully converted into cyclopentanone (**2b**) and cycloheptanone (**2c**) in good isolated yields (entries 1 and 2). What's more, the end point of reaction time could be determined conveniently by observation of the vessel pressure through a barometer. As expected, *o*-, *m*-, *p*-methylcyclohexanol were smoothly oxidized into their corresponding ketones (**2d**, **2e** and **2f**) in 2-2.5 h with excellent selectivity (entries 4-6). 3,3-Dimethylcyclohexanone (**2g**) could be obtained in 98% isolated yield when 3,3-dimethylcyclohexanol (**1g**) was used as the substrate (entry 7). However, 2-octanol (**1h**) was less reactive under the optimal reaction conditions, the conversion was only 66% in 5 h. A full conversion of **1h** with 99% selectivity and 90% yield of 2-octanone (**2h**) was achieved by increasing the amount of both TBN and KPF<sub>6</sub> to 6 mol% (entry 8). Moreover, the substrate containing a phenyl group (**1i**) almost quantitatively afforded **2i** in 99% isolated yield (entry 9).<sup>20</sup>



**Table 2.**  
Oxidation of Secondary Unactivated Alcohols <sup>a</sup>

Entry	Substrate	Product	Time (h)	Conv. <sup>b</sup> (%)	Select. <sup>b</sup> (%)	Yield <sup>c</sup>
1		<b>1a</b> 	<b>2a</b> 1.5	99	99	85
2		<b>1b</b> 	<b>2b</b> 3.5	97	99	83
3		<b>1c</b> 	<b>2c</b> 2	99	99	96
4		<b>1d</b> 	<b>2d</b> 2.5	99	98	90
5		<b>1e</b> 	<b>2e</b> 2	99	99	91
6		<b>1f</b> 	<b>2f</b> 2	99	99	96
7		<b>1g</b> 	<b>2g</b> 2	99	99	98
8 <sup>d</sup>		<b>1h</b> 	<b>2h</b> 3.5	99	98	90
9		<b>1i</b> 	<b>2i</b> 3	>99	99	99

<sup>a</sup> **1** (30 mmol), ABNO (6 mol%), TBN (5 mol%), KPF<sub>6</sub> (4 mol%), water (10 mL), 60 °C (oil bath), O<sub>2</sub> (0.5 MPa).

<sup>b</sup> Conversion and selectivity were determined by GC with area normalization method.

<sup>c</sup> Isolated yield.

<sup>d</sup> TBN (6 mol%), KPF<sub>6</sub> (6 mol%).

With these results in hand, we then focused our studies on the application ABNO/TBN/KPF<sub>6</sub>/O<sub>2</sub> system to a variety of activated alcohols in water. The results are summarized in Table 3. As expected, secondary benzylic alcohols are more reactive compared with secondary aliphatic alcohols.

Acetophenone (**4a**) could be transformed from 1-phenylethanol (**3a**) smoothly when we reduced the amount of ABNO and KPF<sub>6</sub> to 2 mol% and oxygen pressure to 0.3 MPa.<sup>21</sup> Two secondary benzylic alcohols, **3b** and **3c**, bearing electron-donating groups were oxidized to the corresponding ketones (**4b**

and **4c**) efficiently. Moreover, the oxidation of secondary benzylic alcohols with electron-withdrawing groups, such as 1-(4-fluorophenyl)ethanol (**3d**), 1-(4-bromophenyl)ethanol (**3e**) and 1-(4-chlorophenyl)ethanol (**3f**), furnished the expected products (**4d**, **4e** and **4f**) with excellent yields in 2-2.5 h. 1-(3-Chlorophenyl)ethanone (**4g**) was also obtained in 98% isolated yield. However, sterically hindered substrate **3h** containing 2-Cl on phenyl ring showed lower reactivity, only 68% conversion was achieved in 5 h. Notably, 93% isolated yield could be achieved in the case of increasing both loading of ABNO and KPF<sub>6</sub> to 3 mol%. 1-Phenylpropan-1-ol (**3i**) and 1-*p*-tolylpropan-1-ol (**3j**) were transformed smoothly, and almost quantitatively afforded their corresponding ketones (**4i** and **4j**) in 98-99% isolated yields. When 1-(4-chlorophenyl)propan-1-ol (**3k**) was chosen as the substrate, only 31% conversion was obtained in 5 h in the same reaction conditions. To our delight, 93% isolated yield could be achieved (**4k**) with 6 mol% ABNO, 5 mol% TBN, 4 mol% KPF<sub>6</sub> under 0.5 MPa of oxygen pressure in 80 °C. The conversion of 1-phenylbutan-1-ol (**3l**) was 74% in 6.5 h, but it could be improved to more than 99% by increasing loading of ABNO and KPF<sub>6</sub> to 3 mol%. When 2-methyl-1-phenylpropan-1-ol (**3m**) was used as the substrate, the isolated yield of **4m** could be reached to 90% under the optimal reaction conditions of unactivated alcohols. Several other benzylic secondary alcohols including 2,3-dihydro-1*H*-inden-1-ol (**3n**), 1,2,3,4-tetrahydronaphthalen-1-ol (**3o**), diphenylmethanol (**3p**) and 1-(naphthalen-2-yl)ethanol (**3q**) were also tested for the aerobic oxidation in water. It was found that **3o** could quantitatively converted to **4o**. High yields of ketones **4n**, **4p** and **4q** were achieved by enhancing the reaction conditions slightly. However, 1-(thiophen-2-yl)ethanol (**3r**) was difficult to be transformed to

1-(thiophen-2-yl)ethanone (**4r**), 80% yield of **4r** was obtained by increasing loading of ABNO, TBN and KPF<sub>6</sub> to 10 mol% and oxygen pressure to 0.5 MPa.

**Table 3.**  
Oxidation of Secondary Activated Alcohols <sup>a</sup>

Entry	Substrate	Product	Time (h)	Conv. <sup>b</sup> (%)	Select. <sup>b</sup> (%)	Yield <sup>c</sup> (%)
1			2	>99	99	99
2			1.5	97	99	93
3			3.5	99	98	95
4			2	99	99	96
5			2	>99	99	99
6			2.5	99	99	96
7			2.5	99	99	98
8 <sup>d</sup>			3	97	>99	93
9			2	99	99	98
10			4.5	>99	99	99
11 <sup>e,f</sup>			3.5	86	99	84
12 <sup>d</sup>			5	>99	99	99
13 <sup>e</sup>			2.5	99	95	90
14 <sup>d</sup>			2.5	99	99	97

15		<b>3o</b>		<b>4o</b>	4	>99	99	99
16 <sup>f,g</sup>		<b>3p</b>		<b>4p</b>	4	99	96	92
17 <sup>e,f</sup>		<b>3q</b>		<b>4q</b>	3.5	99	95	93
18 <sup>h</sup>		<b>3r</b>		<b>4r</b>	1.5	95	90	80

<sup>a</sup> **3** (30 mmol), ABNO (2 mol%), TBN (5 mol%), KPF<sub>6</sub> (2 mol%), water (10 mL), 60 °C (oil bath), O<sub>2</sub> (0.3 MPa).

<sup>b</sup> Conversion and selectivity were determined by GC with area normalization method.

<sup>c</sup> Isolated yield.

<sup>d</sup> ABNO (3 mol%), KPF<sub>6</sub> (3 mol%).

<sup>e</sup> ABNO (6 mol%), KPF<sub>6</sub> (4 mol%), O<sub>2</sub> (0.5 MPa).

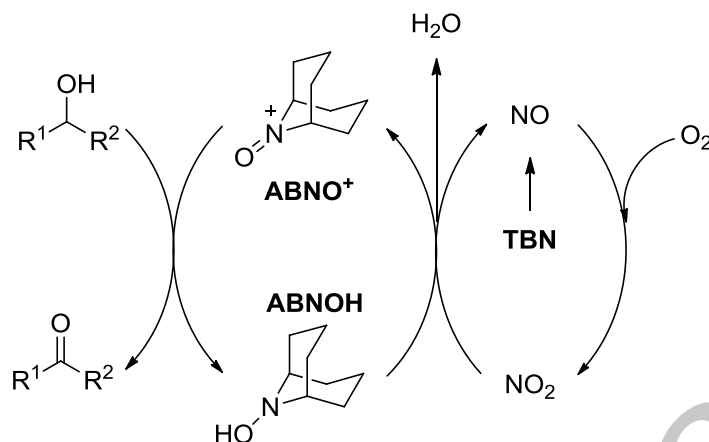
<sup>f</sup> 80 °C.

<sup>g</sup> ABNO (6 mol%), TBN (6 mol%), KPF<sub>6</sub> (6 mol%), O<sub>2</sub> (0.5 MPa).

<sup>h</sup> ABNO (10 mol%), TBN (10 mol%), KPF<sub>6</sub> (10 mol%), O<sub>2</sub> (0.5 MPa).

In addition, this system was also suitable for the oxidation of primary benzylic alcohols into their corresponding aldehydes. With the reaction conditions of 1 mol% ABNO, 5 mol% TBN and 1 mol% KPF<sub>6</sub> in 10 mL water at 60 °C under 0.3 MPa of O<sub>2</sub>, 4-methoxybenzyl alcohol could be oxidized into 4-methoxybenzaldehyde with 97% isolated yields in 3 h. However, when primary aliphatic alcohol, such as cyclohexylmethanol was chosen as the substrate under the optimal reaction conditions of secondary unactivated alcohols, 65% cyclohexanecarbaldehyde along with 34% cyclohexanecarboxylic acid were obtained.

A plausible overall reaction mechanism for the transformation of secondary alcohol into ketone is shown in Scheme 2. Under a certain reaction temperature TBN can release NO, which will be easily oxidized into NO<sub>2</sub> by O<sub>2</sub>. The ABNO is oxidized to ABNO<sup>+</sup> by NO<sub>2</sub>. The alcohol is oxidized to its corresponding ketone by ABNO<sup>+</sup>, which is reduced to ABNOH at the same time. Then ABNOH is oxidized to ABNO<sup>+</sup> by NO<sub>2</sub>, which turns into NO immediately.



**Scheme 2.** A proposed overall reaction mechanism.

In summary, we have successfully applied the ABNO/TBN/KPF<sub>6</sub>/O<sub>2</sub>, a transition-metal free catalytic oxidation system, for the aerobic oxidation of a variety of secondary alcohols in water. This green catalytic oxidation system displayed high reaction efficiency. Numerous ketones could be obtained conveniently in the medium of water.

**Acknowledgement:** This work was financially supported by the National Natural Science Foundation of China (21376224, 21206147), the Natural Science Foundation of Zhejiang Province (LY17B060007), and Hangzhou Qianjiang Distinguished Experts Project.

### Supplementary data

Supplementary data (experimental details and copies of <sup>1</sup>H NMR and <sup>13</sup>C NMR for the products) associated with this article can be found, in the online version, at <http://>.

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20. Typical procedure for aerobic oxidation of secondary unactivated alcohols (Table 2, entry 9): A Teflon-lined 316 L stainless steel autoclave (300 mL) equipped with magnetic stirring bar was charged with 4.51 g of 4-phenylbutan-2-ol (**1i**, 30 mmol), 252.0 mg of ABNO (1.8 mmol, 6 mol%), 154.6 mg of TBN (1.5 mmol, 5 mol%), 220.8 mg KPF<sub>6</sub> (1.2 mmol, 4 mol%) and 10 mL deionized water. The autoclave was closed and charged with oxygen to 0.5 MPa. Then the autoclave was placed into a preheated 60 °C oil bath. The mixture was then stirred for a certain time until the vessel pressure dropped to 0.4 MPa. The autoclave was taken out from the oil bath, cooled to room temperature and carefully depressurized. Most product was obtained directly through simple phase separation. The aqueous phase was extracted with diethyl ether (20 mL×3), the ether layer was then washed with saturated NaCl, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated to dryness. A 99% isolated yield of **2i** was obtained based on the combined product. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.31-7.27 (m, 2H), 7.22-7.19 (m, 3H), 2.93-2.91(m, 2H), 2.79-2.76(m, 2H), 2.15 (s, 3H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 207.8, 140.9, 128.4, 128.2, 126.0, 45.1, 30.0, 29.7.
21. Typical procedure for aerobic oxidation of secondary activated alcohols (Table 3, entry 1): A Teflon-lined 316 L stainless steel autoclave (300 mL) equipped with magnetic stirring bar was charged with 3.66 g of 1-phenylethanol (**3a**, 30 mmol), 84.0 mg of ABNO (0.6 mmol, 2 mol%), 154.6 mg of TBN (1.5 mmol, 5 mol%), 110.4 mg of KPF<sub>6</sub> (0.6 mmol, 2 mol%) and 10 mL of deionized water. The autoclave was closed and charged with oxygen to 0.3 MPa. Then the autoclave was placed into a preheated 60 °C oil bath. The mixture was then stirred for a certain time until the vessel pressure dropped to 0.2 MPa. The autoclave was taken out from the oil bath, cooled to room temperature and carefully depressurized. The mixture was extracted with

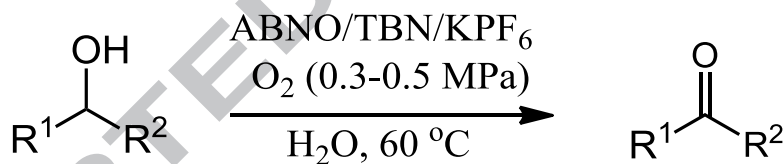
diethyl ether (20 mL×3). Then the combined organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated to dryness, followed by flash column chromatography over silica gel with a mixture of ethyl acetate/petroleum ether as eluent to afford 99% isolated yield of **4a**. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.92-7.90 (m, 2H), 7.52-7.49 (m,1H), 7.42-7.39 (m, 2H), 2.54 (s, 3H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 197.8, 136.9, 132.8, 128.3, 128.0, 26.3.

## Aerobic oxidation of secondary alcohols in water with ABNO/*tert*-butyl nitrite/ $\text{KPF}_6$ catalytic system

Jiaqi Ma, Chao Hong, Yan Wan, Meichao Li, Xinquan Hu, Weimin Mo, Baoxiang Hu, Nan Sun,

Liqun Jin, Zhenlu Shen\*

A green and efficient transition-metal free ABNO/*tert*-butyl nitrite/ $\text{KPF}_6$ -catalyzed aerobic oxidation of secondary alcohols in water has been achieved. Under the optimal reaction conditions, a number of secondary aliphatic alcohols and secondary benzylic alcohols can be converted to their corresponding ketones in excellent yields (up to 99%).



$\text{R}^1$  = alkyl, aryl, hetroaryl ;  $\text{R}^2$  = alkyl, aryl

- transition metal-free
- $\text{O}_2$  as the environmentally benign oxidant
- water as the green solvent
- general: 27 examples, up to 99% isolated yield

**Highlights**

1. Oxidation of secondary alcohols into ketones.
2. ABNO, *tert*-butyl nitrite and  $\text{KPF}_6$  as the catalysts and oxygen as the oxidant.
3. Good to excellent yields can be obtained.
4. Water as the green reaction solvent.
5. Metal-free reaction conditions.