

# A metal-free catalytic system for the oxidation of benzylic methylenes and primary amines under solvent-free conditions†

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Iodine–pyridine–*tert*-butylhydroperoxide is developed as a green and efficient catalytic system for the oxidation of benzylic methylenes to ketones and primary amines to nitriles. The reaction conditions are quite mild and environmentally benign, no transition metals, organic solvents or hazardous reagents being needed. The oxidation of benzylic methylenes gave the corresponding ketones in excellent yields with complete chemoselectivity, while the oxidation of primary amines was complete in several minutes, affording various nitriles in moderate to good yields.

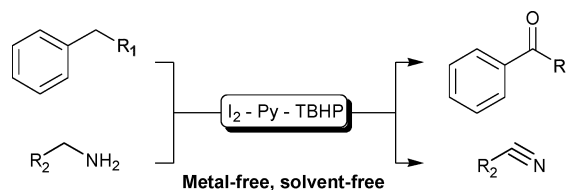
## Introduction

Benzylic oxidation is one of the most useful and important transformations in organic chemistry, and is a powerful tool to generate ketones that not only can serve as valuable building blocks for the manufacture of pharmaceuticals and agrochemicals, but also are integral parts of various natural products.<sup>1</sup> Typically, stoichiometric amounts of metal oxidants, such as potassium permanganate, potassium dichromate or ammonium cerium nitrate were used in the reaction.<sup>2</sup> However, during recent decades, tremendous efforts have been devoted to this transformation, and numerous significant improvements have been achieved. Many metal catalysts have been developed, such as those involving Cr,<sup>3</sup> Mn,<sup>4</sup> Co,<sup>5</sup> Bi,<sup>6</sup> Ru,<sup>7</sup> Rh,<sup>8</sup> and Fe.<sup>9</sup> However, toxic or expensive metal catalysts, hazardous oxidants and organic solvents are still involved in most of these systems. The metal residue and environmental pollution are always the main problem with metal-mediated or metal-catalyzed systems. Therefore, non-metal oxidants, such as IBX, PhIO and NaClO/TBHP, have also been developed for benzylic oxidation,<sup>10</sup> and these gave very good results, although stoichiometric amounts of co-oxidants or environmentally unfriendly by-products were inevitable.

On the other hand, nitriles are versatile intermediates in organic synthesis, which can be easily converted to esters, amides and carboxylic acids. Various methods have been developed for the synthesis of nitrile derivatives,<sup>11</sup> and of these, the preparation of nitriles from primary amines is the most direct and convenient. Over recent decades, many research groups have become interested in the transformation from amines to nitriles, and great achievements have been made. Metal-based oxidants, including metal oxidants<sup>12</sup> and metal catalysts,<sup>13</sup>

behaved very well in oxidizing amines to nitriles. Meanwhile, non-metal systems have also been developed, such as HOCl<sup>14a</sup> and NaOCl,<sup>14b</sup> DIH (1,3-diiodo-5,5-dimethylhydantoin) with aqueous ammonia,<sup>14c,d</sup> TEMPO with TCCA (trichloroisocyanuric acid)<sup>14e</sup> and hyperiodines with additives.<sup>14f-i</sup> Although there are significant improvements in these non-metal systems for the oxidation of primary amines, the catalysts are quite limited. In view of clean synthesis and environmentally benign chemistry, there is therefore a definite need for catalytic systems that can use green oxidants without metals.

As a part of our continued interest in exploring the utility of iodine in organic synthesis,<sup>15</sup> we herein report iodine–pyridine–*tert*-butylhydroperoxide (I<sub>2</sub>-Py-TBHP) as an efficient catalytic system for the oxidation of benzylic methylenes to ketones and primary amines to nitriles (Scheme 1).



**Scheme 1** Iodine–pyridine–*tert*-butylhydroperoxide for the oxidation of benzylic methylenes and primary amines.

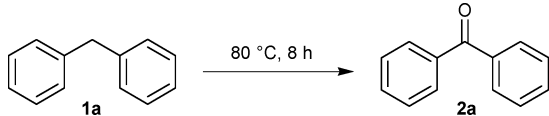
## Results and discussion

### The oxidation of benzylic methylenes to ketones

Initially, the oxidation of diphenylmethane (**1a**) was chosen as a model reaction and the reaction was carried out in pyridine at 80 °C for 8 h. No reaction was observed in the presence of air or oxygen. When H<sub>2</sub>O<sub>2</sub> (30% solution in water) was used, only a trace amount of the product was obtained, and starting material was recovered. However, the employment of a stronger oxidant, aqueous TBHP (70%), enhanced the yield to 16% (Table 1, entry 1). Building upon this result, a variety of iodine sources were examined. From Table 1 it was found that molecular iodine was the best catalyst, and 10 mol% of iodine was enough for this

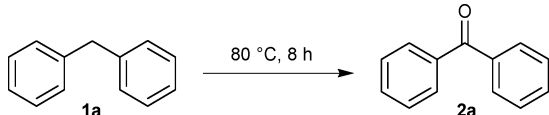
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**Table 1** Optimization of oxidants and iodine resources<sup>a</sup>


Entry	Cat. (mol%)	TBHP (equiv.)	Solvent	Yield (%) <sup>b</sup>
1	—	3.0	Pyridine	16
2	KI (10)	3.0	Pyridine	69
3	Me <sub>4</sub> NI (10)	3.0	Pyridine	85
4	I <sub>2</sub> (10)	3.0	Pyridine	98
5 <sup>c</sup>	I <sub>2</sub> (10)	—	Pyridine	n.d.

<sup>a</sup> Reaction conditions: 0.2 mmol **1a** in 0.2 mL pyridine was heated at 80 °C for 8 h with TBHP and different catalysts. <sup>b</sup> GC yield with internal standard. <sup>c</sup> n.d. = not detected.

**Table 2** Optimization for the benzylic oxidation<sup>a</sup>


Entry	Cat. (mol%)	TBHP (equiv.)	Solvent	Yield (%) <sup>b</sup>
1 <sup>c</sup>	I <sub>2</sub> (10)	3.0	Et <sub>3</sub> N	n.d.
2	I <sub>2</sub> (10)	3.0	Hexane	n.d.
3	I <sub>2</sub> (10)	3.0	THF	n.d.
4	I <sub>2</sub> (10)	3.0	EtOH	n.d.
5	I <sub>2</sub> (10)	3.0	H <sub>2</sub> O	n.d.
6	I <sub>2</sub> (10)	3.0	DCM	5
7	I <sub>2</sub> (10)	3.0	DMSO	10
8	I <sub>2</sub> (10)	3.0	<i>t</i> -BuOH	13
9	I <sub>2</sub> (10)	3.0	MeCN	15
10	I <sub>2</sub> /Py (10/100)	3.0	MeCN	84
11	I <sub>2</sub> /Py (10/50)	3.0	MeCN	87
12	I <sub>2</sub> /Py (10/10)	3.0	MeCN	95
13	I <sub>2</sub> /Py (10/10)	4.0	MeCN	>99
14	I <sub>2</sub> /Py (5/5)	4.0	MeCN	>99
15	I <sub>2</sub> /Py (5/5)	4.0	Neat	>99
16	I <sub>2</sub> /Py (1/1)	4.0	Neat	>99

<sup>a</sup> Reaction conditions: 0.2 mmol **1a** in 0.2 mL solvent was heated at 80 °C for 8 h with catalyst and TBHP. <sup>b</sup> GC yield with internal standard. <sup>c</sup> n.d. = not detected.

reaction in the presence of TBHP (Table 1, entry 4). No product was detected without TBHP (Table 1, entry 5).

Subsequently, the reaction conditions were optimized further. Different solvents were examined to replace pyridine, but no desired product was detected when hexane, triethylamine, THF, ethanol or water were employed (Table 2, entries 1–5). In acetonitrile, 15% yield was obtained, while in CH<sub>2</sub>Cl<sub>2</sub>, DMSO and *t*-BuOH, the yields were 5%, 10% and 13% respectively (Table 2, entries 6–9). This indicated that pyridine was indispensable for this catalytic system, and that acetonitrile was the best solvent. So different amounts of pyridine were tested in the catalytic system, and 95% yield was obtained when the amount of pyridine was reduced to 10 mol% in the presence of 10 mol% of iodine (Table 2, entries 10–12). When TBHP was increased to 4.0 equivalents, the yield increased to 99%. Moreover, in this case the loading of iodine and pyridine could be reduced to 5 mol% without any decrease in yield (Table 2, entries 13 and 14). More importantly, without solvent, the loading of iodine and

pyridine can be reduced further to 1 mol% (Table 2, entries 15 and 16). It is also possible that the reagent TBHP may play the role of solvent in these cases. The reaction temperature was also optimized; below 80 °C the reaction proceeded slowly in a relatively low yield, while no improvement was observed above 80 °C. Finally, the optimized catalytic system was obtained, *viz.* 1 mol% of iodine and 1 mol% of pyridine as a co-catalyst and 4.0 equivalents of aqueous TBHP as an oxidant without solvent at 80 °C (Table 2, entry 15).

With the optimum conditions in hand, we employed the I<sub>2</sub>–Py–TBHP system to investigate the scope of the reaction substrates. It was found that diphenylmethane can provide an isolated yield as high as 95% (Table 3, entry 1). When diarylalkanes bearing fluoro, chloro, bromo and phenyl groups at the *para* position were employed as the reaction substrates, the reaction proceeded smoothly to afford the corresponding products in excellent yields (Table 3, entries 2–5). Moreover, substrates bearing a nitro group (a strong electron-withdrawing group that disfavors aerobic benzylic oxidation mediated by heterogeneous catalysts<sup>16</sup> or the NHPI/Co<sup>2+</sup> system<sup>10e</sup>) were oxidized under our reaction conditions to give the product in a quantitative yield (Table 3, entry 6). This indicated that electron-withdrawing substitution favored this oxidation. When electron-donating groups were installed at the *para* position, the reaction yields decreased a little (Table 3, entries 7 and 8). It is noteworthy that an ester group was also tolerated, and the substrate could be converted to the desired product in good yield (Table 3, entry 9). If the substituents were moved from the *para* position to the *ortho* position or the *meta* position, a slightly negative effect was observed (Table 3, entries 3, 10 and 11). 9H-Fluorene and polycyclic aromatic substrates were converted to the corresponding product smoothly (Table 3, entries 12 and 13). We also tested substrates containing a heterocycle (Table 3, entries 14 and 15). 2-Benzylpyridine, which is a poor substrate for the metal-catalyzed oxidation,<sup>9g</sup> was a good substrate under our reaction conditions, giving the ketone in quantitative yield. Ethylbenzene led to a satisfying result, although the yield decreased with the increase of the alkyl chain (Table 3, entries 16 and 17). Finally, the oxidation procedure was scalable – 10 mmol of **1a** can give **2a** in 93% yield after 24 h.<sup>17</sup>

### The oxidation of primary amines to nitriles

After the successful oxidation of benzylic methylenes to ketones, we explored the iodine–pyridine–*tert*-butylhydroperoxide catalytic system in the oxidation of amines to nitriles.

Benzylamine (**5a**) (1 mmol) was treated with iodine (1 mol%), pyridine (1 mol%) and aqueous TBHP (70%, 2.0 mmol) at 80 °C. After 2 h, the reaction mixture was worked up, and the products found to include 24% of benzonitrile (**6a**) and various by-products as analyzed by GC–MS (Scheme 2).

In spite of the low yield of the desired product, the result inspired us to improve this reaction further. The reaction conditions were optimized, as shown in Table 4.

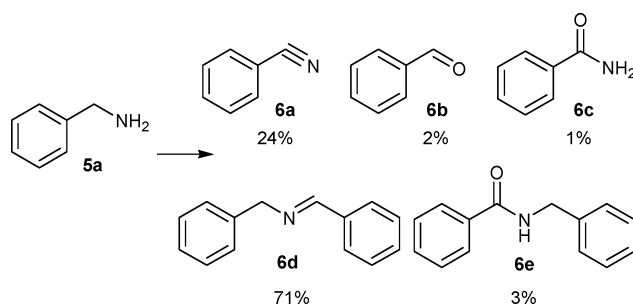
The main product was imine **6d** in Scheme 2, which indicated that the amount of oxidant TBHP was insufficient. When the amount of TBHP was increased to 4.0 equivalents, the yield of benzonitrile was increased to 56% (Table 4, entry 1). No product could be detected without iodine/pyridine or TBHP (Table 4,

**Table 3** The I<sub>2</sub>-Py-TBHP system for benzylic oxidation<sup>a</sup>

Entry	Product	Yield (%) <sup>b</sup>
1	R = H	<b>2a</b> 95 (96) <sup>c</sup>
2	R = <i>p</i> -F	<b>2b</b> 94
3	R = <i>p</i> -Cl	<b>2c</b> 99
4	R = <i>p</i> -Br	<b>2d</b> 97
5	R = <i>p</i> -Ph	<b>2e</b> 94
6	R = <i>p</i> -NO <sub>2</sub>	<b>2f</b> 99
7	R = <i>p</i> -Me	<b>2g</b> 82
8	R = <i>p</i> -OMe	<b>2h</b> 77
9	R = <i>p</i> -OAc	<b>2i</b> 86
10	R = <i>m</i> -Cl	<b>2j</b> 97
11	R = <i>o</i> -Cl	<b>2k</b> 93
12		<b>2l</b> 99
13		<b>2m</b> 73
14		<b>2n</b> 99
15		<b>2o</b> 68
16		<b>2p</b> 90
17		<b>2q</b> 42

<sup>a</sup> Reaction conditions: **1** (1 mmol), I<sub>2</sub> (0.01 mmol), py (0.01 mmol), TBHP (4 mmol), 80 °C, overnight. <sup>b</sup> Isolated yield. <sup>c</sup> 1 equivalent of water was added.

entries 2 and 3). This suggested that iodine/pyridine/TBHP was an integrated catalytic system for this reaction. Subsequently, different solvents were employed in the reaction. In water or in DMSO, the reaction yield decreased to 25%, while in acetonitrile or in DCE the reaction yields reduced to 32% or 33% respectively (Table 4, entries 4, 5, 7, 8). When THF was employed as the reaction solvent, no desired product was obtained at all (Table 4, entry 6). Therefore, no solvent was best. Additives were then

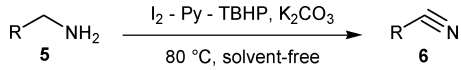
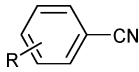
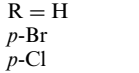
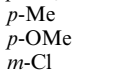
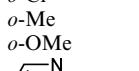
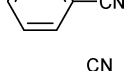
**Scheme 2** The oxidation of benzylamine with the I<sub>2</sub>-Py-TBHP system.**Table 4** Optimization for the oxidations of primary amines<sup>a</sup>

Entry	I <sub>2</sub> /Py (mol%/mol%)	TBHP (equiv.)	Time (min)	Additive	Yield (%) <sup>b</sup>
1	1/1	4.0	120	—	56
2	—	4.0	120	—	Trace
3	1/1	—	120	—	n.d. <sup>c</sup>
4	1/1	4.0	120	— <sup>d</sup>	25
5	1/1	4.0	120	— <sup>d</sup>	32
6	1/1	4.0	120	— <sup>d</sup>	n.d.
7	1/1	4.0	120	— <sup>d</sup>	33
8	1/1	4.0	120	— <sup>d</sup>	25
9	1/1	4.0	120	TsOH	Trace
10	1/1	4.0	120	Na <sub>2</sub> CO <sub>3</sub>	71
11	1/1	4.0	120	K <sub>2</sub> CO <sub>3</sub>	92
12	1/1	4.0	120	Cs <sub>2</sub> CO <sub>3</sub>	92
13	1/1	4.0	120	KOH	Trace
14	1/1	4.0	120	K <sub>3</sub> PO <sub>4</sub>	71
15	1/1	4.0	5	K <sub>2</sub> CO <sub>3</sub>	98
16	1/1	3.0	5	K <sub>2</sub> CO <sub>3</sub>	93
17	1/1	4.0	5	K <sub>2</sub> CO <sub>3</sub> <sup>e</sup>	78
18	<b>0.5/0.5</b>	<b>4.0</b>	<b>5</b>	<b>K<sub>2</sub>CO<sub>3</sub></b>	<b>98</b>

<sup>a</sup> Reaction conditions: **5a** (1 mmol) was heated with I<sub>2</sub>, py, TBHP and the additive (1 equiv.) for the indicated time at 80 °C. <sup>b</sup> GC yield with internal standard. <sup>c</sup> n.d. = not detected. <sup>d</sup> 1 mL of solvent was added: water (entry 4); MeCN (entry 5); THF (entry 6); DCE (entry 7); DMSO (entry 8). <sup>e</sup> 0.5 equiv. of K<sub>2</sub>CO<sub>3</sub> was used.

introduced to the reaction system. TsOH poisoned the catalyst and resulted in the failure of the reaction (Table 4, entry 9), while Na<sub>2</sub>CO<sub>3</sub> gave 71% yield (Table 4, entry 10). Then different carbonates were tested. When 1 equivalent of K<sub>2</sub>CO<sub>3</sub> or Cs<sub>2</sub>CO<sub>3</sub> was added to the reaction mixture, the reaction yield was 92% (Table 4, entries 11 and 12). Considering that potassium salts are cheaper than caesium salts, potassium carbonate was employed as an additive in this reaction. Other potassium salts (such as K<sub>3</sub>PO<sub>4</sub>, K<sub>2</sub>HPO<sub>4</sub>, KOAc and KOH) were also examined, but none of them was better than K<sub>2</sub>CO<sub>3</sub> (Table 4, entries 13 and 14). It was noted that if the reaction was quenched after 5 min when the bubbling had ceased to be obvious, the yield was as high as that after 2 h (Table 4, entry 15). Other oxidants, for example hydrogen peroxide (30% solution in water), were also examined, but resulted in low conversion to **6d**. Decreasing the amount of TBHP had a slight negative influence on the yield, while decreasing the amount of K<sub>2</sub>CO<sub>3</sub> had a dramatic effect (Table 4, entries 16 and 17). Finally, the loading of iodine and pyridine could be reduced to as little as 0.5 mol% (Table 4,

**Table 5** The I<sub>2</sub>-Py-TBHP catalytic system for the oxidation of amines to nitriles<sup>a</sup>

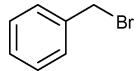
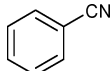
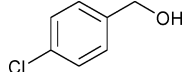
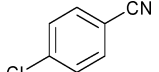
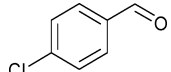
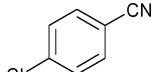
				
Entry	Product		Time/min	Yield (%) <sup>b</sup>
				
1	R = H	<b>6a</b>	5	90
2	<i>p</i> -Br	<b>6b</b>	3	84
3	<i>p</i> -Cl	<b>6c</b>	5	78
4	<i>p</i> -CF <sub>3</sub>	<b>6d</b>	5	81
5	<i>p</i> -Me	<b>6e</b>	5	54
6	<i>p</i> -OMe	<b>6f</b>	6	82
7	<i>m</i> -Cl	<b>6g</b>	5	69
8	<i>o</i> -Cl	<b>6h</b>	6	74
9	<i>o</i> -Me	<b>6i</b>	4	65
10	<i>o</i> -OMe	<b>6j</b>	5	78
11		<b>6k</b>	4	67
12		<b>6l</b>	4	81
13		<b>6m</b>	5	63
14		<b>6n</b>	6	61

<sup>a</sup> Reaction conditions: amine (1 mmol) was heated with I<sub>2</sub> (0.5 mol%), pyridine (0.5 mol%), TBHP (4 equiv.) and K<sub>2</sub>CO<sub>3</sub> (1 equiv.) for the indicated time at 80 °C. <sup>b</sup> Isolated yield.

entry 18). Therefore, the optimum reaction conditions were obtained, *viz.* iodine (0.5 mol%) and pyridine (0.5 mol%) as the catalyst, aqueous TBHP (70%, 4.0 mmol) as an oxidant and potassium carbonate (1 equiv.) as an additive, at 80 °C for 5 min.

With the optimized conditions in hand, we investigated the scope of the reaction substrates, as shown in Table 5. Both benzyl amines and aliphatic amines can be converted into the aromatic nitriles and aliphatic nitriles smoothly in moderate to good yields within several minutes. For instance, benzylamine gave benzonitrile in a yield of 90% (Table 5, entry 1). Benzylamine with different *para*-substituents (such as bromo, chloro, trifluoro, methyl and methoxy) generally gave good results, except for *para*-tolylmethanamine (Table 5, entries 2–6). If the same substituent groups were moved to the *ortho* or *meta* position from the *para* position, the reaction results were almost the same (Table 5, entries 7–10). This indicated that the I<sub>2</sub>-Py-TBHP catalytic system was insensitive to the electronic or steric effects of different substituents. Heteroatomic arylamines and polycyclic arylamines were also suitable substrates in this reaction, giving picolinonitrile and 1-naphthonitrile respectively in good yields (Table 5, entries 11 and 12). Also, the aliphatic amine can be a good substrate in this reaction, affording the corresponding aliphatic nitrile in good yield (Table 5, entry

**Table 6** The oxidation of other substrates to nitriles

Entry	Substrate	Product	Yield (%) <sup>b</sup>
1			99
2			81
3			86

<sup>a</sup> Reaction conditions: substrate (1 mmol) was heated with I<sub>2</sub> (0.5 mol%), Py (0.5 mol%), TBHP (4 equiv.), K<sub>2</sub>CO<sub>3</sub> (1 equiv.) and 28% NH<sub>3</sub>H<sub>2</sub>O (3 equiv.) for 30 min at 80 °C. <sup>b</sup> GC yield with internal standard.

13). As for unsaturated amines, the double bond usually is an active reaction position. In this I<sub>2</sub>-Py-TBHP catalytic system the double bond survived the reaction while the amino functional group was converted into the nitrile smoothly (Table 5, entry 14). Furthermore, the reaction can be scaled up five-fold without a decrease in yield. For example, under the standard reaction conditions, 5 mmol of **5a** was oxidized to give the corresponding nitrile with an isolated yield of 88%.<sup>17</sup>

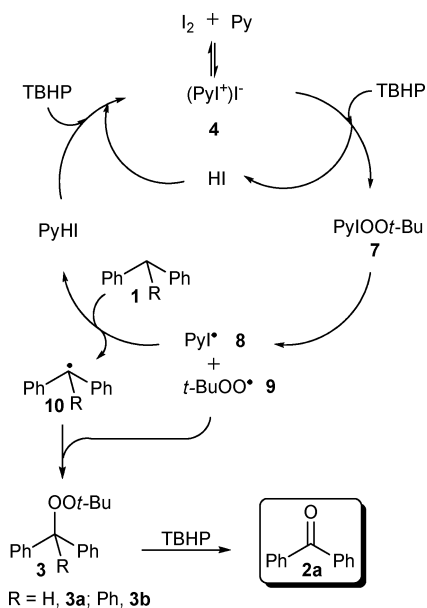
In addition, with this catalytic system, alcohols, aldehydes and alkyl halides can be converted into the corresponding nitriles with good yields in the presence of ammonia.<sup>18</sup> For instance, 1 mmol of reaction substrate was treated with 0.5 mol% of iodine, 0.5 mol% of pyridine, 4 equiv. of aqueous TBHP and 1 equiv. of potassium carbonate in the presence of 3 equiv. of aqueous ammonia at 80 °C for 30 min. It was found that benzyl bromide was almost converted quantitatively to benzonitrile while both (4-chlorophenyl)methanol and 4-chlorobenzaldehyde were transformed into 4-chlorobenzonitrile with yields of 81% and 86% respectively (Table 6).

In summary, the I<sub>2</sub>-Py-TBHP catalytic system is a versatile oxidation system. Using this catalytic system, we can achieve the transformations of benzylic methylenes to ketones, primary amines, alcohols, aldehydes and alkyl halides to nitriles easily. The reaction was carried out under solvent-free and metal-free conditions, avoiding the use of any metallic catalysts or additives. Excellent yields and selectivity were obtained, and this procedure can also be scaled up.

### Studies on the reaction mechanisms

To get an insight into the mechanism for the oxidation of benzylic methylenes to ketones, several control experiments were performed. (1) In the presence of hydroquinone or benzoquinone, the oxidation did not occur and only the starting material was recovered. This implied that the reaction involved a radical pathway. (2) When the reaction was quenched after 30 min, a peroxide **3a** was observed and isolated in a yield of 20% (Scheme 3). When triphenylmethane was employed as starting material, peroxide **3b** was obtained in 49% yield. (3) Peroxide **3a** can be converted to the product in the presence

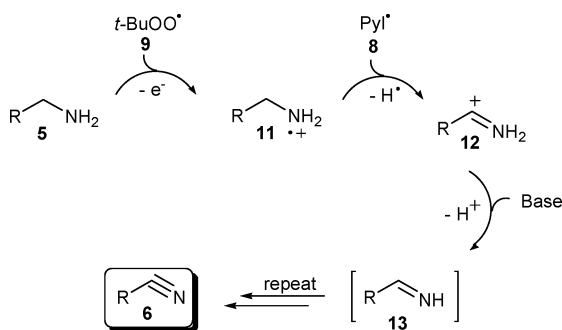




**Scheme 3** Possible mechanism of the  $\text{I}_2$ -Py-TBHP-catalyzed benzylic oxidation.

of TBHP. (4) Diphenylmethanol was not detected during the reaction. When diphenylmethanol was employed as starting material, no conversion was observed. Based on the facts above and previous reports,<sup>19</sup> a possible mechanism was proposed as shown in Scheme 3. When iodine is mixed with pyridine, the “outer complex” **4** appears.<sup>19a</sup> After releasing HI, intermediate **7** is formed, which may generate two kinds of radicals, **8** and **9**. Subsequently, radical **8** activates substrate **1** to give another radical intermediate **10**, which produces peroxide **3** with the *tert*-butylperoxy radical **9**. Finally, the intermediate peroxide **3a** decomposes to **2a** with the assistance of TBHP, while HI and PyHI are immediately oxidized to the “outer complex” **4** by TBHP, completing the catalytic cycle.

As for the transformation of primary amine to nitriles, a possible mechanism is proposed in Scheme 4. Radicals **8** and **9** are generated as described above, and amine **5** is transformed to a radical cation **11** via electron transfer to the *tert*-butylperoxy radical **9**.<sup>20</sup> Then hydrogen abstraction of the methylene group  $\alpha$  to the nitrogen atom is promoted by radical **8**, followed by deprotonation to form the intermediate imine **13**,<sup>21</sup> in which potassium carbonate may play an important role to suppress the by-products as shown in Scheme 2. Repeating these steps would produce the desired product nitrile **6**.



**Scheme 4** Possible mechanism for the oxidation of primary amines.

## Conclusion

In conclusion, we have developed a novel non-metal catalytic oxidation system, consisting of iodine, pyridine and aqueous *tert*-butylhydroperoxide. This is the first example to employ iodine and pyridine as co-catalyst for oxidation reactions. The catalytic system acts as a highly efficient catalytic system for the oxidation of benzylic methylenes to ketones and primary amines to nitriles. No metals, hazardous reagents or organic solvent are involved in the reaction process, and so this is an environmentally friendly catalytic oxidation system. Further investigations into the reaction mechanism and the application of the  $\text{I}_2$ -Py-TBHP catalytic system are now in progress.

## Experimental

### General procedure for the oxidation of benzylic methylenes to ketones

Diphenylmethane (**1a**) (1 mmol), iodine (0.01 mmol), pyridine (0.01 mmol) and aqueous *tert*-butylhydroperoxide (70%, 4 mmol) were sealed in a 20 mL tube, then stirred at 80 °C overnight. After cooling to room temperature, the mixture was purified by a short pad of column chromatography, yielding benzophenone (**2a**) in 95% yield.

### General procedure for the oxidation of amines to nitriles

Amine **5a** (1 mmol), iodine (0.005 mmol), pyridine (0.005 mmol), aqueous *tert*-butylhydroperoxide (70%, 4 mmol) and potassium carbonate (1 mmol) were placed into a tube with a finger condenser, and the tube was placed in a pre-heated oil bath at 80 °C. The liquid refluxed vigorously for several minutes, and the reaction was cooled one minute after refluxing ceased. Then the reaction mixture was worked up by standard procedures, and purified using a silica gel column to give the desired product (**6a**) in 90% yield.

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