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A novel and efficient catalytic system including TEMPO/acetaldoxime/$InCl_3$ for aerobic oxidation of primary amines to oximes

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ABSTRACT

A simple and efficient catalytic system including TEMPO/acetaldoxime/$InCl_3$ for aerobic oxidation of primary amines to corresponding oximes by using toluene as the solvent is described. This practical method can use O_2 as the economic and green oxidant, tolerate a wide range of substrates, which can afford the target oximes in moderate to excellent yields.

Oximes are important intermediates in organic synthesis, which can either be dehydrated to nitriles[1,2] or transformed to amides via an acid catalyzed Beckmann rearrangement,[3] and oximes are also very important ligands in the formation of mono- and polynuclear metal complexes.[4] In addition, oximes are highly crystalline compounds that find applications not only for protection, but also for purification[5] and characterization of carbonyl compounds.[6] Moreover, oximes have been widely utilized in medicine, industry, and analytical chemistry.[7–11] The traditional method for the synthesis of oximes is the reaction of a carbonyl compound with hydroxylamine hydrochloride in the presence of a stoichiometric amount of a base.[12,13] However, this method has some drawbacks to restrict its further application: (1) stoichiometric or excess amounts of hydroxylamine salt cost relative to the respective substrates,[14–17] (2) large amounts of by-products are introduced into oximation reactions,[14–17] and (3) the poor yields of the oximes because the resulting oximes can undergo either dehydration to nitriles or acid-catalyzed Beckmann rearrangement to amides.[17]

Recently, other studies have been performed to obtain oximes via the redox methods under oxidative or reductive conditions including reduction of primary nitroalkanes involving the use of $Se/NaBH_4$, Bu_3SnH, $SnCl_2/PhSH$, or $Au/TiO_2/H_2$;[18,19] aerobic oxidation of primary amines by employing 1,1-diphenyl-2-picryl-hydrazyl (DPPH) and tungstated alumina (WO_3/Al_2O_3) as the catalyst and molecular oxygen as the terminal oxidant; or oxidative nitrogen to carbon rearrangement found in the conversion of anilines to benzaldoximes by treating with $HCHO/H_2O_2$.[20–23] Besides, some works on oxidative ammoniation of carbonyl compound to oximes have also been reported.[24,25] However, these methods have one or more short-comings such as harsh reaction conditions, toxic metal salts, poor yields, or the limited substrates, which adversely affect the applications widely for the synthesis of oximes. So there is obviously a need for better options.

Since the catalytic oxidation of amines is of fundamental importance from both bioorganic and synthetic processes[26,27] various methods have been examined. However, useful methods for catalytic oxidation are limited, because of the sensitivity of amines. Aerobic oxidation under mild conditions is one of the current challenges in view of environmental and economical aspects.[28] In the aspects of environmental, economical, molecular oxygen used as an environmentally benign terminal oxidant is extremely important for the catalytic oxidation of amines.

Herein we report a general and efficient procedure for aerobic oxidation of primary amines to corresponding oximes catalyzed by TEMPO/acetaldoxime/$InCl_3$ and toluene as the solvent. This practical method can use air as the economic and green oxidant, tolerate a wide range of substrates, which can afford the target oximes in moderate to excellent yields.

First, the aerobic oxidation of benzylamine to benzaldoxime was used as the model to screen experimental conditions including

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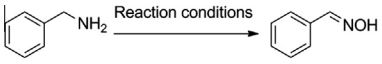
catalyst, additive, TEMPO, bases, solvent, gas, temperature, and time. As shown in Table 1, when the reaction was conducted the aerobic oxidation of benzylamine was catalyzed by TEMPO/acetaldoxime/$InCl_3$ in toluene and the reaction was performed at 100 °C for 4 h. To our delight, the desired benzaldoxime was obtained in 89% yield (Table 1, entry 1). A lower yield was obtained in the absence of one of the TEMPO/acetaldoxime/$InCl_3$ (entries 2–4). Other four metal catalysts also had considerable catalytic activity, among them $InCl_3$ exhibited the highest (entries 5–8). Various acetaldoxime analogues were compared, and we found that acetaldoxime gave the highest yield (entries 1, 9–11). After screening the loadings of TEMPO, acetaldoxime, and $InCl_3$, we found that 10 mol % TEMPO, 5 mol % $InCl_3$ and 3.1 equiv acetaldoxime were the most appropriate proportion (entries 1, 12–18). Solvent screening, demonstrated that Toluene is the best one compared with all the others (entries 1, 19–22). Besides, we also tested the influence of the gas, and we found that the O_2 is significant for the reaction, and O_2 is better than air (entries 1, 23–24). Further optimization by screening the reaction temperature and time showed that 100 °C and 4 h were optimal for this reaction, higher temperatures and longer reaction time do not increase the yields (entries 25–30).

Encouraged by the good catalytic activity, we expanded the scope of the present catalytic system to a series of primary amines under our optimized conditions. As shown in Table 2, a variety of primary amines were examined to the corresponding oximes. The reaction could be successfully applied to a range of different substituted benzylamines and gave the corresponding products in moderate to excellent yields. Benzylamine with either electron-donating or electron-withdrawing groups on the benzene ring smoothly generated the corresponding products in moderate to good yields. Clearly, the reaction conditions were compatible with fluoro, chloro, and bromo substituent groups (entries 2–4). When the benzylamines bear electron-donating substituents, the yield of the aromatic oxime with substituent at *ortho* or *meta* position was slightly lower than those with substituent at the para position (entries 4–9). That may be, in part, due to steric hindrance. Additionally, electronic effects play an important role, as electron-withdrawing substituents (entry 9) on the benzene ring favor the transformation, whereas electron-donating substituents (entries 7, 10–12) objected the transformation. Fortunately, 1-naphthalenemethylamine and 3-phenyl-2-propylene amine could also be successfully converted to the corresponding oximes in good yields in this reaction system (entries 15–16). Moreover, we also conducted heterocyclic primary amines under the employed reaction conditions (entries 17–21). To our surprise, heterocyclic amines show high reactivity to give the corresponding oximes in good yields. To demonstrate the scope and efficiency of the present method, this catalytic system was then extended for the synthesis of aliphatic oximes (entry 22). We found that octylamine could oxidate to octanal oxime in an yield of 38%.

Preliminary mechanistic studies of the reaction were also conducted. First, we turn our attention to the reaction of benzylamine to *N*-benzylidenebenzylamine as shown in Table 3. After optimizing the reaction condition, we found that, almost no *N*-benzylidenebenzylamine occurred in the absence of TEMPO (entries 1 and 4). When TEMPO was added in the reaction, the yield increased up to 56% (entry 2), and reached the highest when 10 mol % acetaldoxime and 10 mol % TEMPO were added (entry 5). Besides, we found that the yield of *N*-benzylidenebenzylamine would decrease in the presence of $InCl_3$ (entries 2, 3, 5, and 6), that may

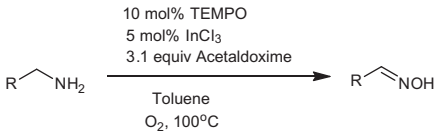
Table 1
Screen of reaction conditions[a]

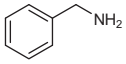
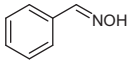
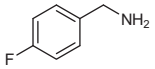
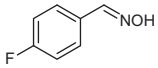
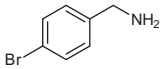
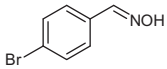
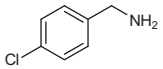
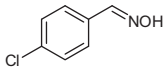
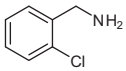
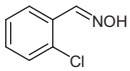
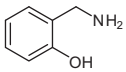
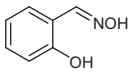
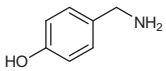
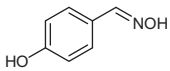
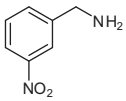
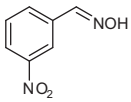
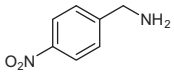
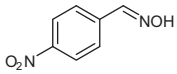
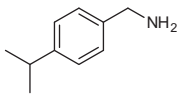
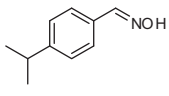
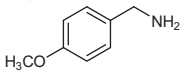
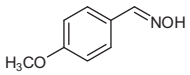
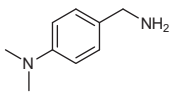
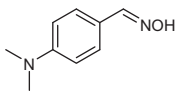
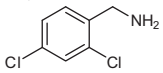
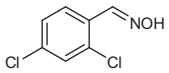
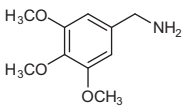
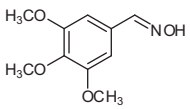
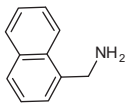
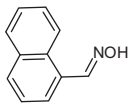
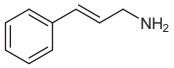
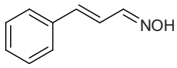
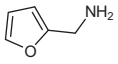
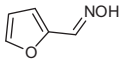
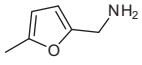
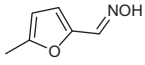
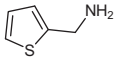
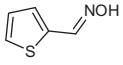
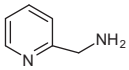


Entry	Catalyst (mol %)	Additive (equiv)	TEMPO (mol %)	Solvent	Gas	T. (°C)	Time (h)	Yield[b] (%)
1	$InCl_3$ (5)	Acetaldoxime (3.1)	10	Toluene	O_2	100	4	89
2	—	Acetaldoxime (3.1)	10	Toluene	O_2	100	4	56
3	$InCl_3$ (5)	—	10	Toluene	O_2	100	4	Trace
4	$InCl_3$ (5)	Acetaldoxime (3.1)	0	Toluene	O_2	100	4	Trace
5	$AlCl_3$ (5)	Acetaldoxime (3.1)	10	Toluene	O_2	100	4	65
6	$ZnCl_2$ (5)	Acetaldoxime (3.1)	10	Toluene	O_2	100	4	52
7	$CuCl_2$ (5)	Acetaldoxime (3.1)	10	Toluene	O_2	100	4	13
8	$FeCl_3$ (5)	Acetaldoxime (3.1)	10	Toluene	O_2	100	4	39
9	$InCl_3$ (5)	Acetoxime (3.1)	10	Toluene	O_2	100	4	77
10	$InCl_3$ (5)	Dimethylglyoxime (3)	10	Toluene	O_2	100	4	61
11	$InCl_3$ (5)	cyclohexanone oxime (5)	10	Toluene	O_2	100	4	75
12	$InCl_3$ (1)	Acetaldoxime (3.1)	10	Toluene	O_2	100	4	65
13	$InCl_3$ (10)	Acetaldoxime (3.1)	10	Toluene	O_2	100	4	89
14	$InCl_3$ (5)	Acetaldoxime (3)	10	Toluene	O_2	100	4	85
15	$InCl_3$ (5)	Acetaldoxime (2)	10	Toluene	O_2	100	4	73
16	$InCl_3$ (5)	Acetaldoxime (5)	10	Toluene	O_2	100	4	89
17	$InCl_3$ (5)	Acetaldoxime (3.1)	5	Toluene	O_2	100	4	88
18	$InCl_3$ (5)	Acetaldoxime (3.1)	20	Toluene	O_2	100	4	89
19	$InCl_3$ (5)	Acetaldoxime (3.1)	10	DMSO	O_2	100	4	Trace
20	$InCl_3$ (5)	Acetaldoxime (3.1)	10	EtOH	O_2	80	4	21
21	$InCl_3$ (5)	Acetaldoxime (3.1)	10	DMF	O_2	100	4	Trace
22	$InCl_3$ (5)	Acetaldoxime (3.1)	10	MeCN	O_2	100	4	Trace
23	$InCl_3$ (5)	Acetaldoxime (3.1)	10	Toluene	Air	100	4	77
24	$InCl_3$ (5)	Acetaldoxime (3.1)	10	Toluene	N_2	100	4	Trace
25	$InCl_3$ (5)	Acetaldoxime (3.1)	10	Toluene	O_2	110	4	89
26	$InCl_3$ (5)	Acetaldoxime (3.1)	10	Toluene	O_2	80	4	84
27	$InCl_3$ (5)	Acetaldoxime (3.1)	10	Toluene	O_2	60	4	69
28	$InCl_3$ (5)	Acetaldoxime (3.1)	10	Toluene	O_2	rt	4	Trace
29	$InCl_3$ (5)	Acetaldoxime (3.1)	10	Toluene	O_2	100	6	89
30	$InCl_3$ (5)	Acetaldoxime (3.1)	10	Toluene	O_2	100	10	89

[a] 1 mmol benzylamine, $InCl_3$, oxime, TEMPO, O_2, 5 ml solvent.
[b] Isolated yields.

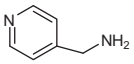
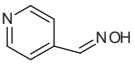
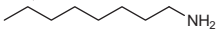
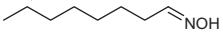
Table 2
Aerobic oxidation of primary amines to oximes catalyzed by TEMPO/acetaldoxime/$InCl_3$[a]



Entry	Benzylamine	Product	T (h)	Yield[b] (%)
1			4	89
2			4	92
3			4	91
4			4	92
5			5	81
6			5	76
7			8	84
8			6	87
9			3	95
10			6	89
11			8	81
12			8	78
13			4	88
14			8	80
15			4	89
16			8	73
17			6	84
18			6	83
19			6	79
20			8	71

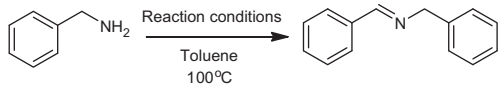
(*continued on next page*)

Table 2 (*continued*)

Entry	Benzylamine	Product	T (h)	Yield[b] (%)
21			8	82
22			12	38

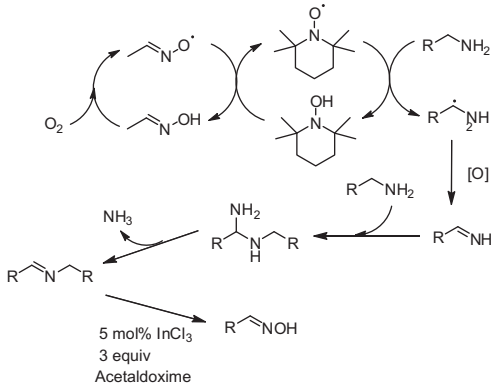
[a] 1 mmol benzylamine, 5 mol % $InCl_3$, 3.1 equiv acetaldoxime, 10 mol % TEMPO, O_2, 5 ml toluene, 100 °C.
[b] Isolated yields.

Table 3
Aerobic oxidation of benzylamine to imine[a]



Entry	Acetaldoxime (mol %)	TEMPO (mol %)	$InCl_3$ (mol %)	Oxidant	Yield[b] (%)
1	—	—	—	O_2	Trace
2	—	10	—	O_2	56
3	—	10	5	O_2	38
4	10	—	5	O_2	Trace
5	10	10	—	O_2	97
6	10	10	5	O_2	75
7	10	10	5	N_2	Trace

[a] 1 mmol benzylamine, $InCl_3$, acetaldoxime, TEMPO, O_2, 5 ml toluene, 100 °C, reaction for 4 h.
[b] Isolated yields.



Scheme 1. A possible reaction mechanism for aerobic oxidation of benzylamine to benzaldoxime.

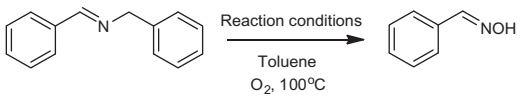
be part of the *N*-benzylidenebenzylamine conversion to benzaldoxime. Then, when we tried to explore the reaction under N_2, the yield of product was trace (entry 7). Therefore, this reaction was an aerobic oxidative step which was catalyzed by acetaldoxime and TEMPO, used O_2 as the oxidant.

By the encouragement of these results, we speculated, in the imine formation step, aerobic oxidation of benzylamine to form *N*-benzylidenebenzylamine. Then, we focused on the oxime formation step: *N*-benzylidenebenzylamine transformed to benzaldoxime, preliminary studies of this conversion were conducted, the result is shown in Table 4. When *N*-benzylidenebenzylamine was treated with 3 equiv acetaldoxime, and 5 mol % $InCl_3$, the desired product was isolated in 88% yield (entry 7). In the absence of one of them, the yield decreased substantially (entries 1, 3, and 5). In addition, a series of experiments show that, TEMPO has no obvious effect on this conversion from *N*-benzylidenebenzylamine to benzaldoxime (entries 2, 4, 6, and 8). Then, we also conducted this conversion under N_2, the yield was decreased slightly (entry 9). Therefore, acetaldoxime and $InCl_3$ were essential for the reaction.

Based on these results and the literature reports about the aerobic oxidation of primary amines to imines,[29–31] a plausible reaction pathway for the formation of benzaldoxime is shown in Scheme 1. The first step of the reaction was to involve the corresponding N-oxyl radical of acetaldoxime, which was formed by the reaction of acetaldoxime and dioxygen. And then this N-oxyl radical abstracted hydrogen from TEMPOH to recover acetaldoxime. Simultaneously, TEMPOH was converted to TEMPO, which oxidated the benzylamine to form benzyl imine. Then benzyl imine reacted with another molecule benzylamine, and generated the intermediary *N*-benzylidene-benzylamine by removing ammonia. Finally, *N*-benzylidenebenzylamine further transforms to afford the product benzaldoxime catalyzed by acetaldoxime and $InCl_3$.

In conclusion, we have developed a simple and efficient catalytic system including TEMPO/acetaldoxime/$InCl_3$ for aerobic oxidation of primary amines to corresponding oximes by using toluene as the solvent. This practical method can use O_2 as the economic and green oxidant, tolerate a wide range of substrates, which can afford the target oximes in moderate to excellent yields.

Table 4
Transformation of imines to oximes[a]



Entry	Acetaldoxime (equiv)	TEMPO (mol %)	$InCl_3$ (mol %)	Gas	Yield[b] (%)
1	—	—	—	O_2	Trace
2	—	10	—	O_2	Trace
3	—	—	5	O_2	10
4	—	10	5	O_2	12
5	3	—	—	O_2	49
6	3	10	—	O_2	52
7	3	—	5	O_2	88
8	3	10	5	O_2	87
9	3	—	5	N_2	85

[a] 1 mmol benzylamine, $InCl_3$, acetaldoxime, TEMPO, O_2, 5 ml toluene, 100 °C, reaction for 4 h.
[b] Isolated yields.

Experimental Section

All starting materials were purchased from commercial sources and used without further treatment. All known compounds were identified by appropriate technique such as ^1H and ^{13}C NMR. NMR (500 MHz) was recorded on a Bruker 500 spectrometer with tetramethylsilane (TMS) as an internal standard. Analytical thin layer chromatography (TLC) was performed on precoated silica gel 60 F254 plates. Yields refer to the isolated yields of the products after purification by silica-gel column chromatography (300 mesh).

General procedure for the aerobic oxidative synthesis of oximes

A mixture of 2 mmol primary amine, acetaldoxime (6.2 mmol), $InCl_3$ (0.1 mmol), TEMPO (0.2 mmol), and Toluene (10 ml) was placed in a 20 ml three-necked flasks. O_2 was bubbled into the flask at a flow rate of 20 ml/min. The reaction mixture was stirred at 100 °C for several hours and the reaction progress was monitored by TLC. After cooling to room temperature, the solution was directly evaporated to dryness and the residue was purified by column chromatography on silica gel (ethyl acetate/n-hexane = 1:8) to give the corresponding oximes.

Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2014.08.083.

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