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NHPI and ferric nitrate: a mild and selective system for aerobic oxidation of benzylic methylenes†

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A mild and selective system comprising *N*-hydroxyphthalimide (NHPI) and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was developed for the oxidation of benzylic methylenes with an atmospheric pressure of molecular oxygen at 25 °C. The influences of reaction conditions such as solvent, different metal catalysts and catalyst loading were studied, as well as the kinetics of the oxidation reaction. Various benzylic methylene substrates could be oxidized to the corresponding carbonyl compounds in satisfactory yields with this catalytic system. Hammett analysis suggested that the substrates with electron-donating groups would have higher oxidation rates. Isotopic (^{18}O) labeling experiments provided evidence of the participation of the nitrate anion in the catalytic cycle. In addition, a possible radical mechanism involving hydrogen atom abstraction by PINO (phthalimide-*N*-oxyl) and nitrate participation for the oxidation of benzylic methylenes in the $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}/\text{NHPI}/\text{O}_2$ system was proposed.

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Introduction

The direct functionalization of C–H bonds has been a long-lasting challenge in modern organic chemistry.¹ Among the techniques employed, oxidation of C–H bonds is one of the most efficient methods to construct carbonyl compounds.² Traditionally, a stoichiometric amount of a hazardous oxidant such as manganese dioxide, potassium dichromate or chromic acid is employed for these transformations, generally generating large amounts of waste and unwanted by-products.³ Molecular oxygen is a convenient and green oxidant for catalytic chemistry due to its economic and environmentally benign features.⁴ However, O_2 is a relatively unreactive oxidant toward the oxidation of inert C–H bonds. Therefore, the direct oxidation of C–H bonds with molecular oxygen as the oxidant is still regarded as one of the main challenges.⁵ To overcome this impediment, various catalysts have been applied to oxygen activation and subsequent C–H bond oxidation.⁶ In recent years, NHPI (*N*-hydroxyphthalimide) has been recognized as a valuable catalyst for the activation of C–H bonds *via* hydrogen abstraction by the intermediate PINO radical.⁷ Also, the formation of the PINO radical from its

precursor NHPI can be achieved by using various mediators, including anthraquinone derivatives, 2,2'-azobisisobutyronitrile (AIBN), oximes, aldehydes, HNO_3 , quaternary ammonium salts, bromine, transition metal salts and so on, with oxygen as the oxidant.^{8–14} In spite of the impressive progress made in this area, oxidation using molecular oxygen as the oxidant under mild conditions is still difficult and the reaction usually occurs at high temperature to overcome the high activation barriers. In addition, oxygen at higher temperature, which exists as a diradical in the ground state, takes part preferably in non-selective radical reactions. Thus, a low temperature may be beneficial for the selectivity of the reaction. However, there are only few reports on achieving the oxidation of C–H bonds involving NHPI as the catalyst at low temperature. Initially, Ishii and co-workers successfully converted alkylbenzenes into the corresponding carboxylic acids under atmospheric dioxygen at ambient temperature using an NHPI and $\text{Co}(\text{OAc})_2$ system in 1997.¹⁵ In addition, Einhorn also reported an efficient system for the aerobic oxidation of benzylic compounds catalyzed by *N*-hydroxy-3,4,5,6-tetraphenylphthalimide (NHTPPI) and CuCl at 35 °C.¹⁶ On the other hand, iron is relatively non-toxic, cheap and environmentally friendly and iron-based catalyst systems have been applied in a variety of organic transformations.¹⁷ Although NHPI combined with iron salts has also been used in various oxidations, such as oxidation of alcohols, oxidative coupling of NHPI with toluene, oxidation of indane in aqueous media and so on, H_2O_2 was used as the oxidant in some systems. Detailed research on the substrate scope, kinetics and mechanism of aerobic oxidation for benzylic C–H bonds has not

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been reported.¹⁸ Our continued efforts in oxidation motivated us to study in detail the use of iron salts as mediators for the transformation of NHPI to PINO, which further achieves the aerobic oxidation of benzylic C–H bonds under mild conditions.¹⁹ Delightedly, by combining NHPI with $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, the aerobic oxidation of benzylic methylenes to the corresponding carbonyl compounds at 25 °C with an atmospheric pressure of molecular oxygen was successfully realized, giving moderate to high yields (Scheme 1).

Results and discussion

Our study commenced with the oxidation of diphenylmethane as the model substrate in the presence of NHPI (5 mol%) at 25 °C with an atmospheric pressure of molecular oxygen, and the screening of different parameters is summarized in Table 1. Initially, the activities of a variety of iron salts were evaluated (Table 1, entries 1–5). Only $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ as the co-catalyst gave moderate conversion and good selectivity (Table 1, entry 5). Further experiments indicated that $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and NHPI were essential to the aerobic oxidation of diphenylmethane (Table 1, entries 6 and 7). The results also suggested that the anions of iron salts had a great effect on the oxidation of diphenylmethane. Subsequently, a series of nitrates were also investigated to test whether there was a certain relationship between the metal cation and the reaction activity (Table 1, entries 8–15). Unfortunately, most of the other nitrates were inert for the oxidation reaction and the substrates were almost recovered (Table 1, entries 9–15). Only in the case of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ as the co-catalyst resulted in a 31% yield of the ketone (Table 1, entry 8). Besides, the effect of the solvents on the oxidation was also evaluated (Table 1, entries 5 and 16–20). The results for screening of the solvents indicated that acetonitrile as the solvent exhibited better catalytic activity compared to the other solvents such as DMSO, dichloromethane, toluene and so on (Table 1, entry 5), perhaps for the retard of the side reaction, such as nitration.²⁰ Taking all these results together, it is the combination of $\text{Fe}(\text{NO}_3)_3$ and NHPI that is necessary to efficiently catalyze benzylic methylene oxidation.

Additionally, the effect of the dosage of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and NHPI was further examined at 25 °C with an atmospheric pressure of molecular oxygen as the oxidant, as listed in Table 2. In the presence of 5 mol% $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and 2 mol% NHPI, only 23% yield was obtained (Table 2, entry 1). The yield reached 72% when the amount of NHPI was increased to 10 mol% (Table 2, entry 3), but almost no change was observed by further increasing the amount of

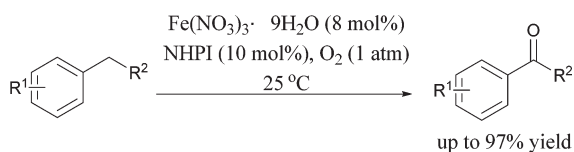
NHPI to 12 mol% (Table 2, entry 4). Therefore, 10 mol% of NHPI is considered as the desired catalyst loading. Further studies indicated that good results were obtained with 8 mol% $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Table 2, entry 5).

With a set of optimized conditions in hand, the scope of the methylene substrates was investigated and the results are tabulated in Table 3. First, a variety of ethylbenzene derivatives containing different substituted groups on the aromatic ring were subjected to the oxidation system with NHPI and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ as the catalysts. The results demonstrated that all the tested ethylbenzene derivatives could be oxidized to the desired ketones in moderate to good yields (Table 3, entries 1–8). For example, the oxidation of 4-ethylbiphenyl provided 83% yield under the optimized conditions (Table 3, entry 7). However, ethylbenzene derivatives bearing OAc or Ph on the methyl group only gave 23% and 24% yields, respectively (Table 3, entries 9 and 10). Notably, diphenylmethane, 9*H*-xanthene and 9*H*-fluorene demonstrated excellent reactivities, providing 84% to 97% yields (Table 3, entries 11–13). In the case of oxidation of neopentylbenzene, the reaction did not take place, perhaps due to the steric hindrance of tertiary butyl (Table 3, entry 14). In addition, tetrahydronaphthalene was oxidized to the corresponding ketone in 50% yield (Table 3, entry 15). A non-activated substrate, cyclooctane, was also tested, and 14% yield of cyclooctanone was observed for the oxidation of cyclooctane catalyzed by the $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ /NHPI system (Table 3, entry 16). Additionally, we compared the reaction outcomes catalyzed by the $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ /NHPI system with those of the NHPI/ $\text{Co}(\text{OAc})_2$ system developed by Ishii in 1997.¹⁵ Obviously, the dosage of $\text{Co}(\text{OAc})_2$ in Ishii's system was very low. The present $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ /NHPI system showed higher selectivity for the production of ketones (Ishii's system, 12% and 17% alcohols as by-products with 47% and 31% 1-(*p*-tolyl)ethan-1-one, respectively).

Furthermore, we studied the kinetics of the oxidation to get some hints for the possible mechanism. Fig. 1 presents the kinetic curves of benzophenone accumulation over reaction time under the optimized experimental conditions. The results also indicated that the rate was fast during the initial 7 h, then reduced gradually.

On the other hand, we determined the dependence of the initial rate of benzophenone formation (W_0) on the concentration of each reagent. The dependence of the oxidation rate on the concentration of NHPI is linear in the range of concentration from 0 to 6.67×10^{-2} M (Fig. 2), similar to the result of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Fig. 3).

The effect of *para*-substituents of ethylbenzene derivatives on the oxidation has also been investigated. The experiments were carried out in CH_3CN (1.5 mL) at 25 °C under an atmospheric pressure of molecular oxygen by mixing equimolar amounts (1 mmol) of *para*-substituted ethylbenzene (*p*-Y- C_8H_{10} , Y = MeO, Me, H, Cl, Br or NO_2) and ethylbenzene catalyzed by NHPI (10 mol%) and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (8 mol%) for 1 hour. The relative rates for these *para*-substituted ethylbenzene derivatives, k_{rel} , were evaluated by monitoring the



Scheme 1 Aerobic oxidation of benzylic methylenes.

Table 1 Screening of metal salts and solvents for the aerobic oxidation of diphenylmethane^a

Entry	Metal salt	Solvent	Conv. ^b (%)	Yield ^b (%)
1	K ₃ [Fe(CN) ₆]	CH ₃ CN	NR ^c	—
2	Fe ₂ (SO ₄) ₃ ·9H ₂ O	CH ₃ CN	3	Trace
3	FeCl ₂ ·4H ₂ O	CH ₃ CN	NR ^c	—
4	FeCl ₃ ·6H ₂ O	CH ₃ CN	28	24
5	Fe(NO ₃) ₃ ·9H ₂ O	CH ₃ CN	74	73
6	—	CH ₃ CN	NR ^c	—
7 ^d	Fe(NO ₃) ₃ ·9H ₂ O	CH ₃ CN	NR ^c	—
8	Cu(NO ₃) ₂ ·3H ₂ O	CH ₃ CN	34	31
9	Zr(NO ₃) ₄ ·5H ₂ O	CH ₃ CN	6	3
10	Al(NO ₃) ₃ ·9H ₂ O	CH ₃ CN	7	4
11	Co(NO ₃) ₂ ·6H ₂ O	CH ₃ CN	5	Trace
12	Mg(NO ₃) ₂ ·6H ₂ O	CH ₃ CN	4	Trace
13	Ni(NO ₃) ₂ ·6H ₂ O	CH ₃ CN	4	Trace
14	Zn(NO ₃) ₂ ·6H ₂ O	CH ₃ CN	3	Trace
15	In(NO ₃) ₃ ·5H ₂ O	CH ₃ CN	4	Trace
16	Fe(NO ₃) ₃ ·9H ₂ O	CH ₂ Cl ₂	9	4
17	Fe(NO ₃) ₃ ·9H ₂ O	Ethyl acetate	25	22
18	Fe(NO ₃) ₃ ·9H ₂ O	Dimethyl sulphoxide	NR ^c	—
19	Fe(NO ₃) ₃ ·9H ₂ O	H ₂ O	NR ^c	—
20	Fe(NO ₃) ₃ ·9H ₂ O	Toluene	NR ^c	—

^a Reaction conditions: diphenylmethane (1 mmol), metal salt (5 mol%), NHPI (5 mol%), acetonitrile (1.5 mL), O₂ (1 atm), 25 °C, 40 h.

^b Determined by GC using biphenyl as an internal standard. ^c NR = no reaction. ^d Without NHPI.

Table 2 The influence of the dosage of Fe(NO₃)₃·9H₂O and NHPI on the aerobic oxidation of diphenylmethane^a

Entry	Fe(NO ₃) ₃ ·9H ₂ O (mol%)	NHPI (mol%)	Conv. ^b (%)	Yield ^b (%)
1	5	2	27	23
2	5	8	63	60
3	5	10	74	72
4	5	12	77	73
5	8	10	84	84
6	10	10	86	85

^a Reaction conditions: diphenylmethane (1 mmol), O₂ (1 atm), acetonitrile (1.5 mL), 25 °C, 40 h. ^b Determined by GC using biphenyl as an internal standard.

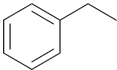
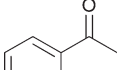
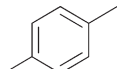
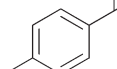
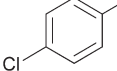
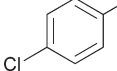
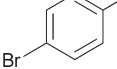
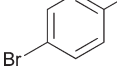
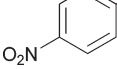
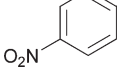
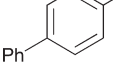
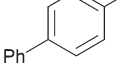
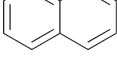
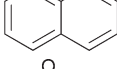
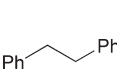
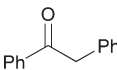
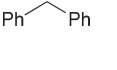
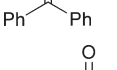
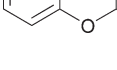
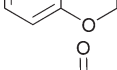
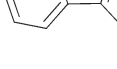
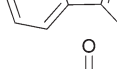
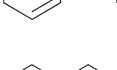
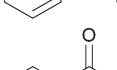
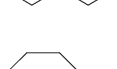
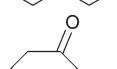
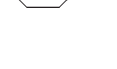
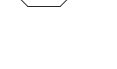


reactions using gas chromatography (Table 4). When the log k_{rel} values determined for each *para*-substituted ethylbenzene were plotted against the substituent constants σ , Hammett correlations were obtained (Fig. 4). A good linear correlation between log k_{rel} and σ [with a negative ρ of -1.3 indicating an electron-demanding transition state] was found, demonstrating the more electron-rich substrates with higher oxidation rates.

In order to further understand the mechanism of the reaction, we have therefore studied the oxidation of diphenylmethane with Fe(NO₃)₃·9H₂O/NHPI under an ¹⁸O₂ atmosphere. The incorporation of ¹⁸O into the products has also been examined (Fig. S1†). The result showed that the percentage of the products containing ¹⁸O was 53%, which indicated that O₂ is not the only oxygen source for the production of benzophenone. Then, we supplemented a blank experiment using diphenylmethane (1 mmol) catalyzed by Fe(NO₃)₃·9H₂O (8 mol%) and NHPI (10 mol%) in 1.5 mL of acetonitrile under argon at 25 °C for 40 h. GC analysis showed that the yield of benzophenone was 30%. The results

indicated that only Fe(NO₃)₃·9H₂O also had a certain oxidation ability and the partial oxygen of the product should derive from nitrate. Moreover, Hulshof *et al.* reported that changes of the valence state of iron and nitrogen oxides existed in the oxidation of benzyl alcohol by iron(III) nitrate.²⁰ Besides, we supplemented a control experiment using diphenylmethane (1 mmol) catalyzed by FeCl₃·6H₂O (8 mol%), NaNO₃ (24 mol%) and NHPI (10 mol%) in 1.5 mL of acetonitrile under O₂ at 25 °C for 40 h. GC analysis showed that the yield of benzophenone was 70%. Then, we replaced NaNO₃ with NaNO₂ and found that the yield of benzophenone decreased to 51%. The results indicate that the nitrate anion plays an important role in the reaction, and NO₃⁻ and NO₂⁻ could be converted into the real intermediate in the process of the reaction.

Accordingly, the iron cation and the nitrate anion were necessary for the reaction. However, the change of the iron cation and the transformation of nitrate with the help of the iron cation have not been clear up to now. According to our experimental results and previous report, we proposed a

Table 3 Selective aerobic oxidation of C–H bonds of various methylenes by NHPI and Fe(NO₃)₃·9H₂O^a

Entry	Substrate	Product	Yield ^b (%)
1			70 ^c
2			79 ^c
3 ^d			57 ^c
4			63 ^c
5			60 ^c
6			54 ^c
7			83
8			51
9			23
10			24
11			84 ^c
12			97
13			90
14			Trace
15			50
16			14 ^c

^a Reaction conditions: substrate (1 mmol), Fe(NO₃)₃·9H₂O (8 mol%), NHPI (10 mol%), acetonitrile (1.5 mL), O₂ (1 atm), 25 °C, 40 h. ^b Isolated yield. ^c Determined by GC using biphenyl as an internal standard. ^d *t* = 20 h.

possible mechanism as shown in Scheme 2. Based on our previous report on the oxidation of alcohols catalyzed by NHPI and Fe(NO₃)₃·9H₂O, Fe³⁺ could be transformed into Fe²⁺ during the reaction detected by addition of K₃[Fe(CN)₆] solution.^{19c} After the reaction, we tested the pH of the system which was indicated to be a weakly acidic environment, probably due to the hydrolysis of hydrated ferric ions (Scheme 2, (1)).^{20a,21} Fe³⁺ has a strong oxidizing ability and Fe²⁺ could be oxidized to Fe³⁺ with the help of O₂ or NO₃⁻ under acidic conditions (Scheme 2, (2) and (3)).²² The reaction may be initiated by hydrogen atom abstraction from the hydroxyimide group of NHPI by the iron compound and N_xO_y under oxygen atmosphere (Scheme 2, (4)).^{12b,22–24} Then, PINO abstracts the hydrogen atom from diphenylmethane to produce the corresponding radical 1, which subsequently reacts with molecular oxygen or NO₂ producing peroxy radical 2 or nitrite 2'.²⁵ Then, intermediate 2 accepts hydrogen to provide 3, which then loses water and is transformed into the desire ketone. The hydroperoxide intermediate 3 may also be transformed into the benzyl alcohol derivative 4, which under further oxidation provides the corresponding ketone. Besides, the desired product could be also produced by the elimination or arrangement of 2'.^{20a}

Experimental

General remarks

All starting materials and catalysts were purchased from commercial suppliers without further purification. ¹⁸O₂ was purchased from Sigma-Aldrich. Column chromatography was generally performed on silica gel (200–300 mesh) and TLC inspections were carried out on silica gel GF254 plates.

GC analysis was performed on an Agilent Technologies 6820 with a flame ionization detector and an HP-5MS column (0.25 mm × 30 m, film: 0.25 μm). GC-MS spectra were recorded on an Agilent Technologies 7890A GC system with an Agilent 5975 inert mass selective detector (EI) and an HP-5MS column (0.25 mm × 30 m, film: 0.25 μm). ¹H NMR and ¹³C NMR spectra were recorded on a Bruker 400 MHz

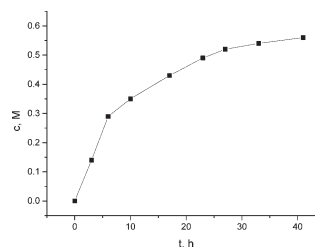


Fig. 1 Benzophenone accumulation in the oxidation of diphenylmethane catalyzed by NHPI (6.67×10^{-2} M) and Fe(NO₃)₃·9H₂O (5.33×10^{-2} M) in the presence of O₂ (1 atm) in acetonitrile.

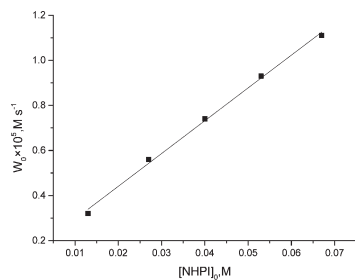


Fig. 2 Dependence of benzophenone initial accumulation rate W_0 on the concentration of NHPI (reaction conditions: diphenylmethane (1 mmol), $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (8 mol%), O_2 (1 atm), acetonitrile (1.5 mL), at 25 °C, 4 h).

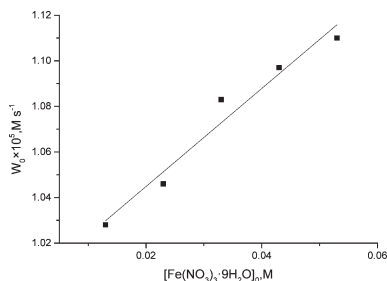


Fig. 3 Dependence of benzophenone initial accumulation rate W_0 on the concentration of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (reaction conditions: diphenylmethane (1 mmol), NHPI (10 mol%), O_2 (1 atm), acetonitrile (1.5 mL), at 25 °C, 4 h).

Table 4 List of k_{rel} and σ values for the oxidation of *para*-substituted ethylbenzene derivatives

Entry	Y	k_{rel}	σ
1	MeO	0.64	-0.27
2	Me	0.31	-0.17
3	H	0	0
4	Cl	-0.19	0.23
5	NO_2	-0.87	0.78

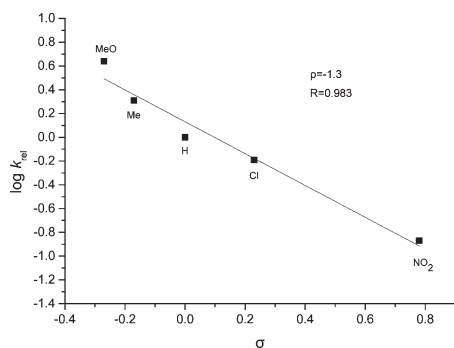
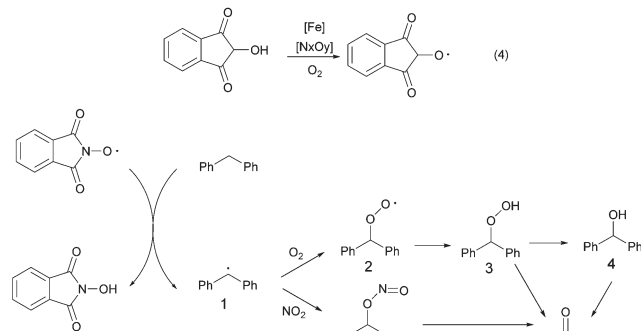
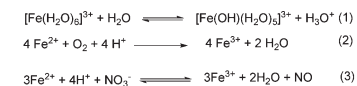


Fig. 4 Hammett correlation studies ($\log k_{\text{rel}}$ vs. σ) for the oxidation of *para*-substituted ethylbenzene derivatives catalyzed by $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and NHPI with an atmospheric pressure of molecular oxygen as the oxidant.

spectrometer using CDCl_3 as the solvent with TMS as an internal reference.



Scheme 2 Proposed mechanism for the oxidation of diphenylmethane catalyzed by NHPI and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ with O_2 .

General procedure for oxidation of benzylic methylenes

The substrate (1 mmol) and the desired amounts of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and NHPI were added to 1.5 mL of acetonitrile in a 15 mL test tube. The solution was stirred for 40 h under an atmospheric pressure of O_2 at 25 °C controlled using a water bath. After the reaction, 30 mg of biphenyl or nitrobenzene as an internal standard was added to the reaction system. The solution was centrifuged and the supernatant was diluted with diethyl ether and dried with anhydrous Na_2SO_4 for 30 minutes. The products were analyzed by GC and further confirmed by GC-MS or NMR. The isolated yield was obtained through column chromatography generally performed on silica gel (200–300 mesh).

Conclusions

We have developed a system including NHPI and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ for the aerobic oxidation of benzylic methylenes at 25 °C in the presence of 1 atm O_2 . Various benzylic methylenes could be oxidized to the corresponding carbonyl compounds in satisfactory yields in this catalytic system. Hammett analysis suggested that the substrates with electron-donating groups would have higher oxidation rates. The isotopic (^{18}O) labeling study provided evidence of the participation of the nitrate anion in the catalytic cycle. In addition, a radical mechanism involving abstraction of the hydrogen atom by PINO as well as dioxygen and nitrate anion participation in the catalytic cycle was proposed. Further investigations toward the scope and mechanism are underway in our laboratory.

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