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Selective Oxidation of Unsaturated Alcohols Catalyzed by Sodium Nitrite and 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone with Molecular Oxygen under Mild Conditions

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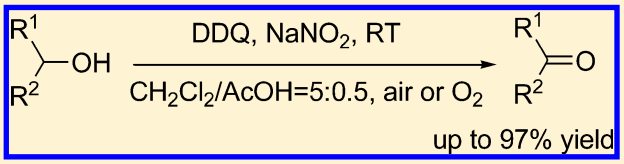
Supporting Information

ABSTRACT: We have developed a simple and practical process for the oxidation of alcohols to the corresponding carbonyl compounds by using a low catalytic amount of DDQ, $NaNO_2$ as a cocatalyst, and molecular oxygen as terminal oxidant. Nitric oxide generated in situ by $NaNO_2$ in the presence of AcOH is essential for the realization of the catalytic cycle at room temperature. The practical utility of this catalytic process has been demonstrated in the gram-scale oxidation of cinnamyl alcohol.



The selective oxidation of alcohols into carbonyl compounds is one of the most important transformations in organic synthetic chemistry.[1] Although traditional methods with stoichiometric amounts of oxidants such as MnO_2, chromium salts, and the Dess–Martin reagent are useful, large amounts of toxic waste are produced.[2] From both economic and environmental viewpoints, the use of green oxidants, such as molecular oxygen as terminal oxidant, is the focus of great attention because dioxygen is inexpensive and water is produced as the only byproduct. However, dioxygen is inert. There is a high energy barrier between organic compounds and dioxygen at room temperature. At higher temperatures, nonselective radical reactions preferentially take place. Although transition metals or transition metal complexes have been shown to be capable of catalyzing the aerobic oxidation of alcohols with molecular oxygen,[3] these methods are still suffering from drawbacks such as the use of expensive noble metals (e.g., Pd, Pt, Ru, Au), or complexes thereof, and commercially unavailable ligands. To address some of these limitations, the development of efficient, transition-metal-free catalytic processes for the aerobic oxidation of alcohols appears very attractive.[4] Our group is particularly interested in this subject.

We were inspired by the ability of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) to act as a highly effective oxidant for many reactions.[5] Although DDQ is an efficient oxidant for the oxidation of alcohols, stoichiometric or even excess amounts of DDQ have been used.[6] Hence, the development of processes requiring only catalytic amounts of DDQ are of great practical relevance. Very recently, Helquist's group reported a catalytic DDQ (20 mol %) catalyzed alcohol oxidation with 6 equiv of $Mn(OAc)_3$ as oxidant.[7] In terms of atom economy and environmental aspects, the use of excess amounts of $Mn(OAc)_3$ as terminal oxidant is undesirable because of large amounts of unwanted byproducts. During the revision of this manuscript, Hu's group reported DDQ/TBN catalytic system for the oxidation of alcohols in 1,2-dichloroethane under 0.2 MPa O_2 at 80 °C.[8] Here, we report a method by which a low catalytic amount of DDQ combined with $NaNO_2$ as a cocatalyst in the presence of AcOH can be successfully used for the room temperature oxidation of alcohols to carbonyl compounds using molecular oxygen as terminal oxidant.

Initially, we selected cinnamyl alcohol as model substrate, using 1 mol % DDQ in CH_2Cl_2 under O_2 atmosphere (balloon) in the presence of 10 mol % $NaNO_2$ at room temperature. The yield of cinnamaldehyde was only 5% (Table 1, entry 1). When a solvent mixture of CH_2Cl_2/AcOH (5/0.1, v/v) was used, cinnamaldehyde was obtained in 24% yield after 2 h (Table 1, entry 2). This very promising result indicated that AcOH apparently plays an important role for obtaining a good catalytic activity.[9] By increasing the amount of AcOH, a yield of 92% cinnamaldehyde was obtained in a CH_2Cl_2/AcOH (5/0.5, v/v) solvent mixture (Table 1, entry 3). A good result could also be obtained in toluene/AcOH (Table 1, entry 4). Other solvents such as CH_3CN/AcOH, THF/AcOH, dioxane/AcOH, and ethyl acetate/AcOH showed a poor performance under otherwise identical reaction conditions (Table 1, entries 5–8). When the amount of DDQ was reduced to 0.5 mol %, cinnamaldehyde was obtained in 75% yield (Table 1, entry 9). The presence of $NaNO_2$ was also considered, and we discovered that 10 mol % of $NaNO_2$ were optimal (Table 1, entries 10, 11). The catalytic system showed poor reactivity without DDQ or $NaNO_2$ (Table 1, entries 12, 13). Another important advantage of this catalytic system is that an air atmosphere in place of a dioxygen balloon also results in good yields (Table 1, entries 14, 15). It was also found that AcOH as a solvent is effective (Table 1, entry 16).

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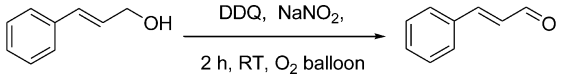
Table 1. Optimization of the Oxidation Conditions



entry	DDQ (mol %)	$NaNO_2$ (mol %)	solvent (v/v)	yield[a] (%)
1	1	10	CH_2Cl_2	5
2	1	10	CH_2Cl_2/AcOH(5/0.1)	24
3	1	10	CH_2Cl_2/AcOH(5/0.5)	92
4	1	10	toluene/AcOH(5/0.5)	68
5	1	10	THF/AcOH(5/0.5)	6
6	1	10	ethylacetate/AcOH(5/0.5)	27
7	1	10	CH_3CN/AcOH (5/0.5)	7
8	1	10	dioxane/AcOH(5/0.5)	14
9	0.5	10	CH_2Cl_2/AcOH(5/0.5)	75
10	1	5	CH_2Cl_2/AcOH(5/0.5)	89
11	1	2.5	CH_2Cl_2/AcOH(5/0.5)	79
12		10	CH_2Cl_2/AcOH(5/0.5)	5
13	1		CH_2Cl_2/AcOH(5/0.5)	5
14[b]	1	5	CH_2Cl_2/AcOH(5/0.5)	74
15[b]	1	10	CH_2Cl_2/AcOH(5/0.5)	89
16	1	10	AcOH	84

[a]Determined by GC using internal standard. [b]Under air atmosphere.

Having identified the optimized reaction conditions, we turned our attention to the examination of scope and limitation of this catalytic oxidation system. The results are summarized in Table 2. The results in Table 2, entries 1−3 indicate that our catalytic system shows high reactivity toward conjugated allylic alcohols. There are only a few reports on the aerobic oxidation of propargylic alcohols.[10] α-Acetylenic carbonyl compounds are very useful precursors in organic synthesis. In the present catalytic system, the oxidation of propargylic alcohols could afford the desired products in excellent yields (Table 2, entries 4−8). Alcohols having only α-hydrogens were converted to the corresponding aldehyde in 95% yield (Table 2, entry 4). It was found that propargylic alcohols with an arylic substituent in the 3-position show high reactivity (Table 2, entries 5, 6). We also studied longer reaction times, and the loading of $NaNO_2$ was increased to 20 mol % for 1-phenylprop-2-yn-1-ol oxidation (Table 2, entry 6). The aliphatic propargylic alcohol hex-4-yn-3-ol was less reactive, affording the corresponding ketone in 20% yield by prolonging the reaction time and increasing the loading of $NaNO_2$ to 20 mol % (Table 2, entry 9). Next, the oxidation of benzylic alcohols was examined (Table 2, entries 10−18). Benzyl alcohols with methoxy substitution were converted to the corresponding aldehydes in excellent yields (Table 2, entries 10−13). 3,4-Dimethoxybenzyl alcohol, a lignin model compound, could be successfully oxidized into the desired product in 96% yield (Table 2, entry 10). Benzyl alcohols with hydroxyl substitution in the *p*-position served as good substrates and afforded the desired products in good yields, which indicated that hydroxyl substitution on the phenyl group was unaffected at the reaction conditions (Table 2, entries 14, 15). 4-Methylbenzyl alcohol was converted to 4-methylbenzaldehyde in 53% yield. The improvement of the yield was observed in the case of using 10 mol % of DDQ (Table 2, entries 16, 17). 9-Hydroxyfluorene was converted to provide the corresponding ketone in good yield (Table 2, entry 19). Electron-deficient benzylic alcohols showed low reactivity. Only a 6% yield of 4-chlorobenzaldehyde was obtained (Table 2, entry 20). Compared with allylic, propargylic, and electron-rich benzylic alcohols, saturated aliphatic alcohols failed to afford the desired products (Table 2, entries 21, 22).

Next we used the DDQ/$NaNO_2$ catalytic system for selective oxidation of alcohols (Table 3). When a mixture of cinnamyl alcohol and benzyl alcohol was used, cinnamyl alcohol was fully consumed, whereas only 2% of the benzyl alcohol was oxidized. The same feature was observed for a mixture of cinnamyl alcohol and 1-phenylethanol. Similarly, for a mixture of 3-phenylprop-2-yn-1-ol and benzyl alcohol, 94 and 7% conversions were obtained after 10 h, respectively. The competing reaction between 3-phenylprop-2-yn-1-ol and 1-phenylethanol showed 96% conversion of 3-phenylprop-2-yn-1-ol, whereas only 10% conversion of 1-phenylethanol was obtained. The oxidation of a mixture of cinnamyl alcohol and 4-methoxybenzyl alcohol was also investigated, and the conversions were 100 and 15%, respectively. These results clearly indicate that allylic and propargylic alcohols could be oxidized selectively in the presence of benzylic alcohols. In addition, to address the selectivity between allylic and propargylic alcohols, a mixture of cinnamyl alcohol and 3-phenylprop-2-yn-1-ol was used. Cinnamyl alcohol was fully consumed, whereas only 9% of the 3-phenylprop-2-yn-1-ol was oxidized. To address a comparison of primary versus secondary propargylic alcohols, the competing reaction between 3-phenylprop-2-yn-1-ol and 1-phenylhex-1-yn-3-ol showed 100% conversion of 1-phenylhex-1-yn-3-ol, whereas only 35% conversion of 3-phenylprop-2-yn-1-ol was obtained.

Finally, the practical applicability of this catalytic system is also demonstrated. We used cinnamyl alcohol as a test substrate and worked on a gram scale.[11] A 50 mmol (6.7 g) reaction of cinnamyl alcohol was performed with 2 mol % of DDQ and 3 mol % of $NaNO_2$ in AcOH under oxygen atmosphere (balloon) at room temperature. The desired product was obtained in 85% yield within 22 h. These results suggest that our system is a highly active, selective, and practical process for aerobic alcohol oxidation.

On the basis of our work and the pertinent literature,[4c,5g,12,13] a plausible overall mechanism for the present aerobic alcohol oxidation is shown in Scheme 1. By combining two redox

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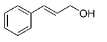
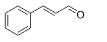
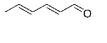
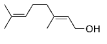
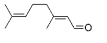
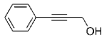
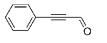
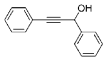
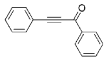
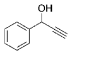
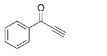
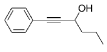
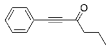
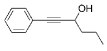
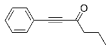
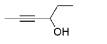
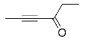
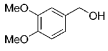
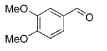
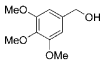
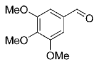
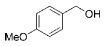
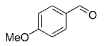
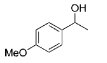
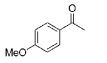
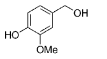
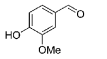
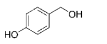
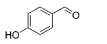
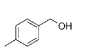
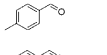
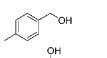
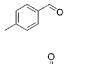
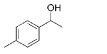
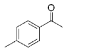
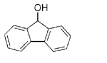
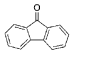
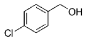
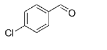
Table 2. Oxidation of Alcohols Catalyzed by DDQ/$NaNO_2$[a]

Entry	Substrate	Product	DDQ (mol%)	Time (h)	Yield[b] (%)
1			1	2	92
2[c,d]			20	20	70
3[c,d]			20	20	17
4			10	10	95
5			5	6	94
6[d]			10	30	84
7			3	10	82
8			5	6	97
9			10	30	20
10			5	6	96
11			5	6	92
12			5	5	97
13			5	8	97
14			3	5	90
15			3	5	90
16			5	18	53
17			10	18	83
18			10	18	87
19			10	8	78
20			10	12	6
21			20	12	0
22			20	12	0

[a]Reaction conditions: alcohols (1 mmol), DDQ, $NaNO_2$ (10 mol %), CH_2Cl_2/AcOH (5/0.5), rt, O_2 balloon. [b]Yields are given for isolated products. [c]AcOH as a solvent. Determined by GC. [d]20 mol % $NaNO_2$.

Table 3. Selective Oxidation of Alcohols Mixtures Catalyzed by DDQ/$NaNO_2$[a]

Entry	Substrates	Products	Conversion[b](%)
1[c]			100 2
2[c]			100 2
3[d]			94 7
4[d]			96 10
5[c]			100 15
6[c]			100 9
7[e]			35 100

[a]Reaction conditions: alcohols (1 mmol each), DDQ, $NaNO_2$ (10 mol %), rt, O_2 balloon. [b]Determined by GC. [c]1 mol % DDQ, 2 h. [d]10 mol % DDQ, 10 h. [e]5 mol % DDQ, 3 h.

Scheme 1. Proposed Catalytic Cycle for the Aerobic Oxidation

couples, DDQ/$DDQH_2$ and NO_2/NO, the selective oxidation of alcohols to carbonyl compounds is achieved with molecular oxygen as terminal oxidant. It is proposed that $NaNO_2$ releases NO in the presence of AcOH,[12a,b] and then NO is easily oxidized by dioxygen to form NO_2. DDQ is the catalytic oxidant, oxidizing alcohols to the desired products. The reduced $DDQH_2$ is subsequently regenerated by NO_2, leading to DDQ and NO. Finally, NO can be reoxidized to NO_2 by dioxygen, thus completing the catalytic cycle.

In conclusion, we have developed a mild, simple, practical, transition-metal-free catalytic process for the aerobic oxidation of alcohols. The oxidation is carried out with catalytic amounts of DDQ/$NaNO_2$ in the presence of AcOH under air or dioxygen atmosphere (balloon) at room temperature. Propargylic alcohols can also be smoothly converted into the corresponding aldehydes or ketones in high yields. In addition, this catalytic system can be very effective for the oxidation of lignin model compounds. Moreover, our newly developed catalytic process shows a high chemoselective oxidation of allylic and propargylic alcohols over benzylic alcohols. Very importantly, the catalytic system is very easy to handle. The success of a catalytic amount of DDQ with a cocatalyst $NaNO_2$ under acidic conditions for the aerobic alcohol oxidation might also be useful for other DDQ-mediated reactions.

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EXPERIMENTAL SECTION

Typical Procedure for the Oxidation of Cinnamyl Alcohol. DDQ (2.3 mg, 0.01 mmol) was dissolved in 5 mL of CH_2Cl_2 and 0.5 mL of AcOH. The solution was stirred open to air at ambient temperature, and then cinnamyl alcohol (134.1 mg, 1 mmol) was added, followed by $NaNO_2$ (6.9 mg, 0.1 mmol). The solution was stirred under dioxygen atmosphere (balloon) for 2 h. The reaction mixture was loaded directly on a small pad of silica, and the product was eluted with dichloromethane. The solvent was concentrated in vacuo, and the product was further purified by column chromatography over silica gel (*n*-hexane/ethyl acetate, 10:1) to afford cinnamaldehyde (121.5 mg, yield, 92%).

Large-Scale Reaction Procedure for the Oxidation of Cinnamyl Alcohol.[11] *One-Gram Reaction, CH_2Cl_2/AcOH Mixture as Solvent.* To a 100 mL, three-necked flask was added DDQ (16.9 mg, 0.0746 mmol), 37 mL of CH_2Cl_2, and 3.7 mL of AcOH. The solution was stirred open to air at ambient temperature, and then cinnamyl alcohol (1 g, 7.46 mmol) was added, followed by $NaNO_2$ (25.7 mg, 0.373 mmol). The solution was stirred under dioxygen atmosphere (balloon). The reaction was monitored by TLC. After completion of the reaction, the reaction mixture was loaded directly on a small pad of silica, and the product was eluted with dichloromethane. The solvent was concentrated in vacuo, and the product was further purified by column chromatography over silica gel (*n*-hexane/ethyl acetate, 10:1) to afford cinnamaldehyde (0.886 g, yield, 90%).

AcOH as Solvent. To a 25 mL, three-necked flask was added DDQ (16.9 mg, 0.0746 mmol) and 5 mL of AcOH. The solution was stirred open to air at ambient temperature, and then cinnamyl alcohol (1 g, 7.46 mmol) was added, followed by $NaNO_2$ (25.7 mg, 0.373 mmol). The solution was stirred under dioxygen atmosphere (balloon). The reaction was monitored by TLC. After completion of the reaction, the reaction mixture was loaded directly on a small pad of silica, and the product was eluted with dichloromethane. The solvent was concentrated in vacuo, and the product was further purified by column chromatography over silica gel (*n*-hexane/ethyl acetate, 10:1) to afford cinnamaldehyde (0.866 g, yield, 88%).

Cinnamaldehyde.[14] Table 2, entry 1, light yellow liquid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.55−6.61 (m, 1H), 7.28−7.35 (m, 4H), 7.40−7.43 (m, 2H), 9.55 (d, $^3J_{H,H}$ = 8.0 Hz, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 128.2, 128.3,128.8, 131.0, 133.7, 152.7, 193.6.

Phenylpropiolaldehyde.[15] Table 2, entry 4, yellow liquid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (t, $^3J_{H,H}$ = 7.6 Hz, 2H), 7.45 (t, $^3J_{H,H}$ = 8.0 Hz, 1H), 7.57 (d, $^3J_{H,H}$ = 7.2 Hz, 2H), 9.38 (s, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 88.3, 95.1,119.2, 128.6, 131.2, 133.1, 176.8.

1,3-Diphenyl-2-propyn-1-one.[16] Table 2, entry 5, yellow liquid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (t, $^3J_{H,H}$ = 7.6 Hz, 2H), 7.51−7.43 (m, 3H), 7.60 (t, $^3J_{H,H}$ = 7.6 Hz, 1H), 7.66 (d, $^3J_{H,H}$ = 7.2 Hz, 2H), 9.38 (s, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 86.8, 93.0,119.9, 128.5, 128.6, 129.4, 130.7, 132.9, 134.0, 136.7, 177.8.

1-Phenyl-2-propyn-1-one.[15] Table 2, entry 6, yellow solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.44 (s, 1H), 7.49 (t, $^3J_{H,H}$ = 7.6 Hz, 1H), 7.63 (t, $^3J_{H,H}$ = 7.2 Hz, 1H), 8.16 (d, $^3J_{H,H}$ = 8.0 Hz, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 80.2, 80.7, 128.7, 129.6, 134.5, 136.1, 177.3.

1-Phenylhex-1-yn-3-one.[17] Table 2, entry 8, orange liquid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.973 (t, $^3J_{H,H}$ = 7.2 Hz, 3H), 1.73−1.78 (m, 2H), 2.60−2.63 (m, 2H), 7.36 (d, $^3J_{H,H}$ = 6.4 Hz, 2H), 7.41 (d, $^3J_{H,H}$ = 6.0 Hz, 1H), 7.54 (d, $^3J_{H,H}$ = 7.2 Hz, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 13.2, 17.4, 47.1, 87.6, 90.2, 119.8, 128.4, 130.4, 132.7, 187.8.

3,4-Dimethoxybenzaldehyde.[14] Table 2, entry 10, light yellow acicular crystal: ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.84 (s, 3H), 3.85 (s, 3H), 6.87 (d, $^3J_{H,H}$ = 8.0 Hz, 2H), 7.34 (d, $^3J_{H,H}$ = 8.4 Hz, 2H), 9.73 (s, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 55.6, 55.3, 108.6, 110.1, 126.5, 129.8, 149.3, 154.2, 190.6.

3,4,5-Trimethoxybenzaldehyde.[18] Table 2, entry 11, pale yellow solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.92 (s, 6H), 3.93 (s, 3H) 7.12 (s, 2H), 9.86 (s, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 56.2, 61.0, 106.7, 131.7, 153.6, 191.0.

4-Methoxybenzaldehyde.[14] Table 2, entry 12, light yellow liquid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.88 (s, 3H), 7.00 (d, $^3J_{H,H}$ = 8.8 Hz, 2H), 7.83 (d, $^3J_{H,H}$ = 8.8 Hz, 1H), 9.88 (s, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 55.2, 114.0, 129.6, 131.6, 164.3, 190.5.

1-(4-Methoxyphenyl)ethanone.[19] Table 2, entry 13, light yellow solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.47 (s, 3H), 3.78 (s, 3H), 6.85 (d, $^3J_{H,H}$ = 8.4 Hz, 2H), 7.85 (d, $^3J_{H,H}$ = 8.4 Hz, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 26.1, 55.2, 113.5, 130.1, 130.4, 163.3, 196.6.

4-Hydroxybenzaldehyde.[20] Table 2, entry 15, light yellow acicular crystal: ^{1}H NMR (400 MHz, DMSO) δ 6.93 (d, $^3J_{H,H}$ = 8.8 Hz, 1H), 7.76 (d, $^3J_{H,H}$ = 8.8 Hz, 2H), 9.78 (s, 1H), 10.58 (s, 1H); ^{13}C NMR (100.6 MHz, DMSO) δ 116.0, 128.6, 132.3, 163.5, 191.1.

4-Methylbenzaldehyde.[14] Table 2, entry 17, colorless liquid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.44 (s, 3H), 7.33 (d, $^3J_{H,H}$ = 8.0 Hz, 2H), 7.77 (d, $^3J_{H,H}$ = 8.0 Hz, 2H), 9.96 (s, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 22.5, 130.3, 130.4, 134.8, 146.1, 192.6.

4-Methylacetophenone.[21] Table 2, entry 18, light yellow liquid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.35 (s, 3H), 2.52 (s, 3H), 7.20 (d, $^3J_{H,H}$ = 8.4 Hz, 2H), 7.81 (d, $^3J_{H,H}$ = 8.4 Hz, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 21.3, 26.2, 128.1, 128.9, 134.4, 143.6, 197.5.

9-Fluorenone.[22] Table 2, entry 19, yellow solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, $^3J_{H,H}$ = 7.2 Hz, 2H), 7.50−7.44 (m, 4H), 7.64 (d, $^3J_{H,H}$ = 7.2 Hz, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 120.2, 124.2,128.9, 134.0, 134.5, 144.3, 193.8.

ASSOCIATED CONTENT

Supporting Information

^{1}H and ^{13}C NMR spectra of the isolated products. This material is available free of charge via the Internet at http://pubs.acs.org.

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(9) Xu and co-workers[5d] reported $NaNO_2$ as an electron-transfer mediator between DDQ and molecular oxygen, which was used to catalyze the oxidative dehydrogenation of 9,10-dihydroanthracene to anthracene in toluene under 1.3 MPa O_2 at 120 °C. However, the coupled $NaNO_2$/DDQ catalyst system gave poor results for alcohol oxidation in toluene under oxygen atmosphere at room temperature, which might be due to slow $NaNO_2$ decomposition to NO_x at room temperature. In addition, Bao's group reported that hydrobenzoquinone was rapidly reoxidized to quinone in CF_3COOH.[12c] $NaNO_2$ is a ready availability source of NO under acidic conditions.[12a,b]

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(11) First, 5 mmol of cinnamyl alcohol were reacted with 1 mol % DDQ, 10 mol % $NaNO_2$ in CH_2Cl_2/AcOH (5/0.5) under oxygen atmosphere (balloon) to give cinnamaldehyde in 64% yield. This poor result might be due to the small amount of AcOH in the solvent mixture. Therefore, AcOH was used instead of CH_2Cl_2/AcOH (5/0.5) under otherwise identical reaction conditions. To our delight, the desired product could be isolated in 90% yield. The dramatic improvement of the yield indicates that AcOH as solvent is essential for this aerobic oxidation system. It has to be noted that good results could also be obtained when the amount of CH_2Cl_2/AcOH solvent mixture was increased with the amount of substrate in the same proportion. Because the large amount of CH_2Cl_2 needed in the large-scale reaction was not economic, we choose AcOH as the solvent for large-scale reactions.

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