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Cobalt(II)-catalyzed benzylic oxidations with potassium persulfate in TFA/TFAA†

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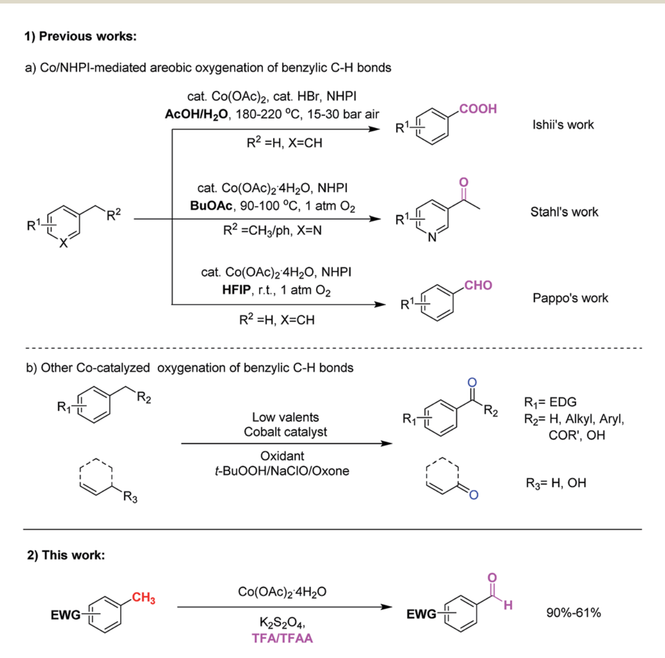
A cobalt-catalyzed C(sp^3)–H oxygenation reaction to furnish aldehyde was herein reported. This transformation demonstrated high chemo-selectivity, and tolerated various methylarenes bearing electron-withdrawing substituents. This reaction provided rapid access to diverse aldehydes form methylarenes. Notably, TFA/TFAA was used for the first time as a mixed solvent in cobalt-catalyzed oxygenation of benzylic methylenes.

Introduction

Benzylic oxidative reaction is one of the most useful and important C–H functionalization in synthetic organic chemistry due to its wide application in the manufacture of pharmaceuticals and chemicals,[1] and these transformations are able to construct various functional groups such as ketone, aldehyde, hydroxyl, carboxylic, ester *etc.* Numerous approaches for the C(sp^3)–H benzylic oxygenation to the corresponding carbonyl derivatives have been developed.[1,2] Traditional methods involving the use of stoichiometric amounts of metallic reagents such as $KMnO_4$, Cr(VI) or potassium dichromate[2a] are common. In the past few decades, many efforts have been devoted to develop oxidation processes catalyzed by transition metals, such as Mn,[3] Cr,[4] Fe,[5] Cu,[6] Bi,[7] Rh,[8] Ru,[9] Pd,[10] Re,[11] Au[12] and V[13] species among others.[14], and fruitful progresses have been achieved.

With the development of C–H functionalization that catalyzed by low-cost and environmentally benign first-row transition metals,[15] various cobalt-catalyzed direct benzylic or allylic oxidation reactions have been reported (Scheme 1).[16–21] Pioneered by Ishii *et. al.*, cobalt-catalyzed C–H(sp^3) oxidation with *N*-hydroxyphthalimide (NHPI) has proven to be a valuable method for the preparation of ketones from alkylarenes and benzoic acids form methylarenes.[16] Following this strategy, Stahl's group reported that benzylic methylene groups in pharmaceutically relevant heterocyclic substrates could be effectively converted into the corresponding ketones by the cobalt(II)/*N*-hydroxyphthalimide (NHPI) catalyst system.[17] Recently, Pappo and co-workers also revealed the unique chemoselectivity for aerobic autoxidation of methylarenes to benzaldehydes based on *N*-hydroxyphthalimide (NHPI) and cobalt(II) acetate in 1,1,1,3,3,3-hexafluoropropan-2-ol (HFIP). The fluorinated alcohol and benzaldehyde may form a H-bond adduct that markedly slow down H-abstraction of the aldehydic C–H bond.[18] It is worth mentioning that this strategy address the long-standing selectivity problem of generating benzaldehydes directly from methylarenes under sustainable conditions.

Other cobalt-catalyzed systems such as TEMPO/$Co(OAc)_2$,[19] *tert*-butyl hydroperoxide/$Co(acac)_2$,[20] and oxone/$Co(ClO_4)_2$ (ref. 21) were developed for the allylic and benzylic oxidation of alkylarenes and methylarenes. The desired ketones derivatives



Scheme 1 Cobalt-catalyzed C–H functionalization (benzylic and allylic oxidation reactions).

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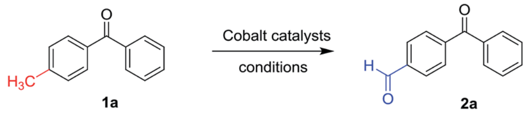
are effectively obtained under these conditions. However, the large excess of oxidants were often required. In addition, the typically more reactive aldehydes are generally difficult to prepare directly from the corresponding methylarenes under most of the above methods.

Despite these significant advancements made in the area of low-valent cobalt-catalyzed benzylic oxygenation, but the selective oxidation of methylarenes to form benzaldehydes is still very challenging. Moreover, the efficiency of C(sp^3)–H benzylic oxygenation were severely restricted by the electronic property of additional substituents on the aryl ring. With the aryl rings bearing electron-donating groups, the corresponding C(sp^3)–H benzylic oxygenation smoothly occurred. While electron-withdrawing groups on the aryl rings generally hampered this transformation.[16–21] Up to date, the direct C(sp^3)–H benzylic oxygenation reactions for the preparation of benzaldehyde that could tolerate with electron-withdrawing groups on the aryl ring are still rare. In consequence, the discovery of a new method for direct benzylic oxidation tolerated with electron-withdrawing groups on the aryl ring would be of considerable importance. Herein, we report a new method for the direct benzylic C(sp^3)–H bond oxidation through cobalt catalysis to afford a series of corresponding aldehydes. This method manifests highly chemo-selectivity, and tolerates with various methylarenes bearing electron-withdrawing substituents. The reaction employs the low cost $Co(OAc)_2 \cdot 4H_2O$ as the catalyst, $K_2S_2O_8$ as the oxidant and TFA/TFAA as the co-solvent.

Results and discussion

We commenced our study with the benzylic oxidation reaction of 4-methylbenzophenone (**1a**) in the presence of 20 mol% of $Co(OAc)_2 \cdot 4H_2O$ as the catalyst, 2.0 equiv. of $K_2S_2O_8$ as the oxidant in TFA/TFAA (6 : 4) co-solvent system at 100 °C. Under this condition, **2a** could be obtained in 12% isolated yields. Initially, we examined this reaction in the presence of a mixted solvents of TFA/TFAA, the aldehyde product **2a** was observed in less than 5% yield with the ratio 5 : 5 of TFA/TFAA (entry 2) and 36% yield with the ratio 9 : 1 of TFA/TFAA at 40 °C (entry 5). But the reaction did not occur in TFA as single solvent (entry 6). The results suggest that the ratio of TFA/TFAA play a key role in this reaction. The high proportion of TFA could dramatically improve the conversion of benzylic oxidation, and TFAA might be involved in the initiation step of cobalt-catalyzed C–H bond cleavage process.[8c,22] When the reaction was performed at 80 °C, the yield dramatically increased to 78% (entry 9). Further experiments revealed that other cobalt catalysts such as $CoBr_2$ and CoF_3 were inferior to $Co(OAc)_2 \cdot 4H_2O$ (entry 10–12), and the benzylic bromination product was observed when $CoBr_2$ was used as a catalyst. As a control reaction, the benzylic oxidation could not occur in the absence of $Co(OAc)_2 \cdot 4H_2O$ (entry 13). Among the oxidants investigated, $Na_2S_2O_8$ was less efficient than $K_2S_2O_8$ (entry 10). $(NH_4)_2S_2O_8$ was much more powerful than $K_2S_2O_8$. However, the decomposition was observed when $(NH_4)_2S_2O_8$ was used instead of $K_2S_2O_8$ (entry 11). The commonly applied oxidants NFSI and $PhI(OAc)_2$ were proved to be inactive (entry 7–8). In general, 20 mol% of $Co(OAc)_2 \cdot 4H_2O$ was enough to catalyze this transformation, the process

Table 1 Optimizing the reaction conditions of benzylic oxygenation[a]

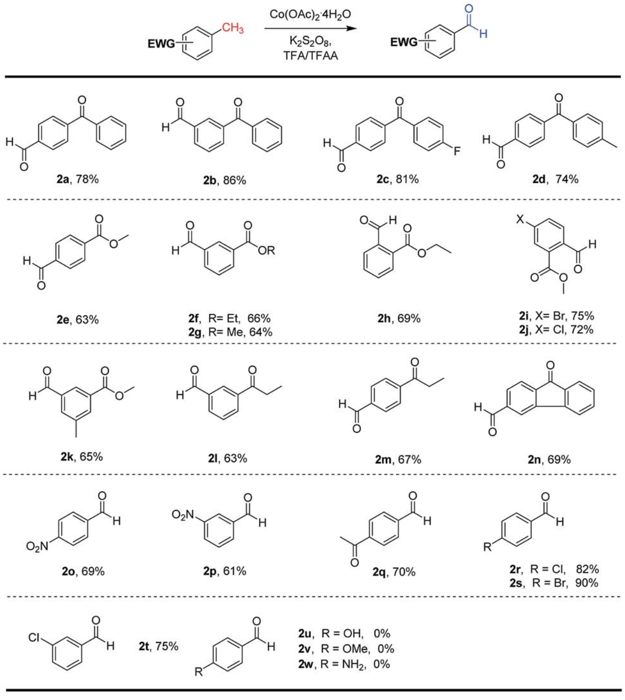


Entry	Cobalt source (mol%)	Oxidants	TFA/TFAA ratio	Temperature	Yield
1	$Co(OAc)_2 \cdot 4H_2O$	$K_2K_2O_8$	6 : 4	100 °C	12%[b]
2	$Co(OAc)_2 \cdot 4H_2O$	$K_2S_2O_8$	5 : 5	40 °C	<5%[c]
3	$Co(OAc)_2 \cdot 4H_2O$	$K_2S_2O_8$	7 : 3	40 °C	21%[c]
4	$Co(OAc)_2 \cdot 4H_2O$	$K_2S_2O_8$	8 : 2	40 °C	29%[c]
5	$Co(OAc)_2 \cdot 4H_2O$	$K_2S_2O_8$	9 : 1	40 °C	36%[b]
6	$Co(OAc)_2 \cdot 4H_2O$	$K_2S_2o_8$	10 : 0	50 °C	<5%[c]
7	$Co(OAc)_2 \cdot 4H_2O$	NFSI	9 : 1	80 °C	N.O.[d]
8	$Co(OAc)_2 \cdot 4H_2O$	$Phl(OAc)_2$	9 : 1	80 °C	N.O.[d]
9	$Co(OAc)_2 \cdot 4H_2O$	$K_2S_2o_8$	9 : 1	80 °C	78%[b]
10	$Co(OAc)_2 \cdot 4H_2O$	$Na_2S_2O_8$	9 : 1	80 °C	41%[b]
11	$Co(OAc)_2 \cdot 4H_2O$	$(NH_4)_2S_2O_8$	9 : 1	80 °C	52%[c]
12	$CoCl_2$	$K_2S_2O_8$	9 : 1	80 °C	19%[c]
13	CoF_3	$K_2S_2O_8$	9 : 1	80 °C	<5%[c]
14	$CoBr_2$	$K_2S_2O_8$	9 : 1	80 °C	15%[c]
15	Without catalysis	$K_2S_2O_8$	9 : 1	80 °C	N.O.[d]

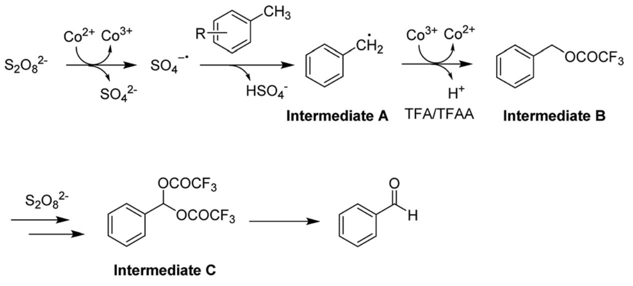
[a] Note: Reaction condition: 1 (0.1 mmol), cobalt catalyst (0.02 mmol), oxidant (0.15 mmol, 1.5 eq.), TFA and TFAA (1 mL). [b] Isolated yield. [c] When the conversion are less than 50%, the conversion ratio was detected by ^{1}H-NMR. [d] N.O. means no observation.

typically went to completion within 10 h with 2.0 equivalents of $K_2S_2O_8$ at 80 °C Table 1.

Having identified the optimal conditions for the direct C(sp^3)–H benzylic oxygenation, we set out to explore the substrates scope for this new reaction. As illustrated in Scheme 2, a range of substituted benzylic substrates were investigated. The scope of methylarenes was broad, and the transformation was smoothly occurred to selectively generate the corresponding aldehydes in moderate to good yields. Aryl groups with different substituent groups, such as Cl, Br, NO_2, acetyl, were tolerated under the optimal conditions. The various substituted methylbenzophenones (**2a–2d**) were successfully oxidized into the desired aldehydes with good yields (78–86%). Interestingly, we found that 4,4′-dimethyl-benzophenone (**2d**) and methyl 3,5-dimethylbenzoate (**2k**) were selectively oxidized to give mono-oxidation products in 74% and 65% yields, respectively. To our delight, a range of methylbenzoates and methylpropiophenones bearing with electron-withdrawing groups (–NO_2, –Br, –Cl) were smoothly transformed into the corresponding aldehydes in moderate to good yields (61–70%). Unfortunately, the electron-rich substituted methylarene substrates, such as *p*-toluidine, 1-methoxy-4-methylbenzene and *p*-cresol, could not be converted the aromatic aldehydes (**2u**, **2v** and **2w**) due to some side-reactions (Friedel–Crafts reaction, acylation *etc.* see ESI†) under the optimal conditions. It was revealed that the electronic property of substituents on methylarene derivatives displayed important effects on the reaction efficiency, and this strategy prefers to the electron-deficient methylarenes. As mentioned before, the electron-deficient methylarenes are difficult to be oxidized under the previous reported conditions,[2,18–21] because the electron-withdrawing groups lead to the benzylic C(sp^3)–H more inert. It is worth pointing out that our method provides a new access for the selective oxidation of the electron-deficient methylarenes to prepare benzaldehydes. To explore the practical utility of this C(sp^3)–H benzylic oxygenation reaction, a gram-scale reaction of methyl 5-bromo-2-methylbenzoate oxidation was performed (Scheme 2) under the standard conditions. The oxidation product **2i** could be obtained in 69% yield with 20 mol% of cobalt catalyst, which demonstrated scalable and practical of this protocol.



Scheme 2 Substrate scope of cobalt(II)-catalyzed C(sp^3)–H benzylic oxygenation.



Scheme 3 Proposed mechanism cobalt(II)-catalyzed C(sp^3)–H oxygenation.

Previous reports proposed that a $SO_4^{\cdot-}$ radical was generated *in situ* in the presence of cobalt.[21,23] Based on literatures,[23] a plausible mechanism for this oxidation process was proposed as shown in Scheme 3. Firstly, the reactions involved the oxidation of Co^{2+} with peroxydisulfate ($S_2O_8^{2-}$) to generate a $SO_4^{\cdot\cdot}$ radical *in situ*.[23a-b] Then the radical reacted with methylarenes to give the radical intermediate **A** radical assisted by the TFA/TFAA solvents, followed by the reduction of Co^{3+} to provide the intermediate **B** that could be detected when the reaction was proceeded at ambient temperature (see ESI†). Following with the second C–H oxidation, the intermediate **C** was generated, which could be further converted to the desired product after a hydrolytic process. Very recently, Fyokin and co-workers demonstrated highly polar trifluoroacetic acid could be an efficient solvent for the metal-free aerobic NHPI-catalyzed oxidations of toluene.[24] In our study, the reaction cannot occur when TFA/TFAA solvent system was replaced with $AcOH/Ac_2O$ under the standard conditions.

Conclusions

In summary, we developed a new protocol for the preparation of benzylaldehydes from the corresponding methylarenes by the direct oxygenation of benzylic C(sp^3)–H. The method shows high chemo-selectivity, and tolerates with various electron-withdrawing substituted arenes, esters and ketones. The TFA/TFAA solvent is first used as a mixed solvent in cobalt-catalyzed oxidation of methylarenes to benzaldehydes.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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