



Cite this: *RSC Adv.*, 2017, 7, 15176

Received 9th January 2017
 Accepted 27th February 2017

DOI: 10.1039/c7ra00352h

rsc.li/rsc-advances

TBHP-promoted direct oxidation reaction of benzylic C_{sp}³–H bonds to ketones†

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A metal-free oxidation system employing *tert*-butyl hydroperoxide (TBHP) has been developed for selective oxidation of structurally diverse benzylic sp³ C–H bonds. This low-cost methodology allows for rapid generation of synthetically and biologically valued arylketones in good to excellent yields from readily available alkylarenes and diarylmethanes.

C–H bond activation reactions have become one of the most important classes of reactions in organic synthesis, the synthetic scope and utility of which has advanced considerably during the past decade.¹ Undoubtedly, there are fundamental benefits for integrating such a strategy in organic synthesis, especially from the vantage point of environmental benignity and high atom/step economy. Furthermore, the construction of complex organic molecules nowadays can be designed in a more direct and effective fashion as these C–H functionalization transformations are an established piece in synthetic organic chemists' toolbox.¹ Among this progress, the direct oxidation of C–H bonds for the synthesis of functionalized molecules has been of great interest in both academic and industrial settings.² Many C–H oxidation methods have thus been developed to date.

Aryl ketones are widely recognized as key functional and structural motifs in a large plethora of significant molecules, including natural products, active pharmaceutical ingredients, agrochemicals and advanced materials (Fig. 1). Also, they frequently serve as useful precursors for the synthesis of complicated organic molecules.³ The classical methods to assemble such motifs involve the Friedel–Crafts acylation⁴ and transition metal catalyzed coupling reactions,⁵ which often suffer from poor selectivity and require harsh reaction conditions as well as toxic or expensive metal salts. In this way, direct benzylic C_{sp}³–H oxidation reactions, as we proposed, could be a more ideal synthetic pathway.⁶ However, the literature survey suggested that most of the existing methods relied on less sustainable oxidants, such as potassium permanganate or chromium acid derivatives.⁷ The resulting vast metal residue not only caused operational challenges upon scale-up, but were

also known as potential carcinogens, and long-term exposure to those hazardous metals might lead to central nervous system disorders.⁸ Consequently, less toxic, cost-effective and sustainable oxidants like peroxides or molecular oxygen, have drawn increasing research interest.

In recent years, considerable progress has been made in this field.⁹ The group of Pandey and Lei independently reported a C–H aerobic oxidation approaches *via* photo-redox chemistry to synthesize aryl ketones.¹⁰ In addition, Li and Wang's group achieved the benzylic C–H oxidation by developing a recyclable TEMPO catalyst.¹¹ Moreover, in 2016, Stahl *et al.* employed the electrochemical *N*-hydroxyphthalimide (NHPI) system to achieve benzylic oxygenation reaction to prepare (hetero)aryl ketones.¹² Very recently, our group also reported a simple and efficient potassium *tert*-butoxide promoted (hetero)benzylic C–H oxidation reaction using oxygen as oxidant.¹³ Our approach provided a ready access to versatile diarylketones under mild conditions. While similar to most of other benzylic oxidation protocols, alkylbenzenes were unfortunately not amenable substrates in that report.¹⁴ Therefore, further research is highly necessary, as direct oxidative C–H functionalization of diverse substrates are still challenging and reported examples are limited in terms of substrate types. Since one of our lab's long-term goal is to

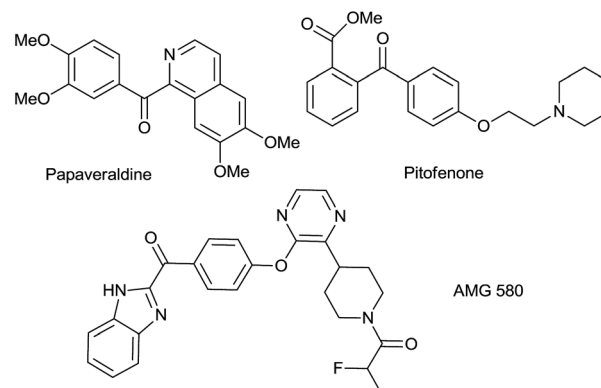


Fig. 1 Selected aryl ketones.

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† Electronic supplementary information (ESI) available. See DOI: 10.1039/c7ra00352h



Table 1 Reaction condition optimization^a

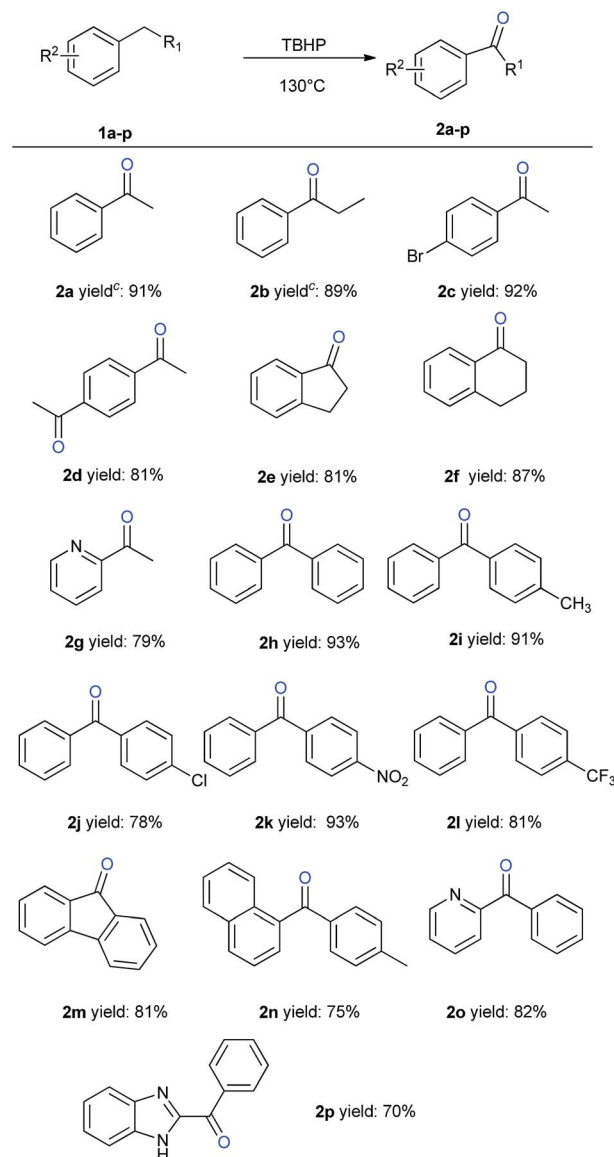
Entry	Oxidant	Yield ^b (%)
1	(NH ₄) ₂ S ₂ O ₈	n.r.
2	K ₂ S ₂ O ₈	n.r.
3	<i>m</i> -CPBA	n.r.
4	DTBP	n.r.
5	CHP	68%
6	Dicumyl peroxide	89%
7	BPO	82%
8	TBHP	91%
9 ^c	TBHP	31%
10 ^d	TBHP	51%

^a Ethylbenzene (1 mmol) and oxidant (12 mmol) were reacted at 130 °C for 10 h. Hexane is the solvent if the oxidant is solid. ^b Determined by GC with internal standard mesitylene. ^c TBHP (3 mmol) was used instead. ^d Reaction temperature was 100 °C.

develop efficient oxidation methods to construct valuable molecules, we herein would like to report our recent efforts in developing a simple and efficient *tert*-butyl hydroperoxide (TBHP) promoted benzylic sp³ C–H oxidation reaction to make aryl ketones.¹⁵

We began our studies by evaluating the oxygenation of ethylbenzene (**1a**) to acetophenone (**2a**), which proved to be challenging in our prior work.¹³ Key results of condition optimization are briefed in Table 1. The initial search for suitable oxidation conditions indicated that persulfates were ineffective oxidants (entries 1–2). We then moved to organic oxidizing agents. A wide array of peroxides and peroxy acids was thus examined (entries 3–8), among which, we were glad to find that the desired product **2a** could be obtained with a superior 91% yield in the presence of TBHP (entry 8). Further investigation revealed that the amount of oxidizing agents is crucial to the reaction outcome, as the desired oxidation product was obtained with only 31% yield when 3 equivalents of TBHP was employed instead. It's also worth mentioning a decreased reaction temperature is detrimental to the rate of the oxidation step as well as the chemical yield, which is probably due to a reduced rate of radical generation step *via* thermal decomposition. Only moderate yield was attained when the transformation was performed at 100 °C (51% yield, entry 10).

With these optimized conditions in hand, we next began an exploration of the substrate scope. As revealed in Scheme 1, the benzylic C–H oxidation transformation could smoothly convert alkylarenes to the corresponding aryl ketones in excellent yields (**2a–2c**). 1,4-Diacetylbenzene (**1d**), which is a common building blocks for fluorophore type compound,¹⁶ could be obtained from corresponding starting material in 81% yield. Next, cyclic alkylarenes such as 2,3-dihydro-1*H*-indene (**1e**) and 1,2,3,4-tetrahydronaphthalene (**1f**) were employed to deliver the target ketone



Scheme 1 Substrate scope.^{ab} Alkylarene or diarylmethane (1 mmol), TBHP (hexane solution, 2 ml, ~12 equiv.), 130 °C in pressure tube. ^b Isolated yields. ^c GC yields.

products in 81% and 87% yields respectively. Furthermore, diarylmethanes were compatible substrates, and reacted under the standard conditions to give the diarylketones (**2h–2l**) in good to excellent yields. In general, both the electron-donating and electron-withdrawing substitution groups had little effects on the chemical yields of oxidation products (**2h–2l**). In addition, fluorene (**1m**) proved to be suitable substrate, giving fluorenone (**2m**) in 81% yield. Notably, this oxidation protocol was discovered to be slightly sensitive to the steric hindrance at *ortho*-position of aromatic ring as 1-naphthyl substituted diarylmethane substrate (**1n**) displayed lower reactivity to give only 75% yield to the desired ketone product **2n**. Given the importance and synthetic challenges of nitrogen-containing heterocycles, we were delighted to find that pyridyl substituted substrate also reacted under this metal-free oxidation conditions to give the heteroaryl



ketone **2g** and **2o** in good yields. Noteworthy, these pyridine-containing substrates often showed poor reactivity under metal-mediated benzylic oxidation reaction, which is probably due to the product inhibition *via* chelation.¹² Finally, these optimized reaction conditions were examined for the oxygenation of pharmaceutically relevant imidazole substrates. 2-Benzoyl-1*H*-benzimidazole (**2p**), the core structural motif of potent phosphodiesterase inhibitor AMG 580, could be directly prepared in 70% yield.^{3f}

To expand the synthetic utility of this oxidative protocol, we then tested other benzylic sp³ C–H compounds as substrates. Under the identical reaction conditions, 2-phenylacetophenone (**2q**) underwent the oxidation reaction to give the benzoic acid (**3q**) instead of the desired benzyl product in 70% isolated yields (Scheme 2).^{10b}

The scale-up synthesis of **2h** also highlighted the utility and operational simplicity of this procedure. When the reaction was run at one-gram scale with diphenylmethane (**1h**), the product (**2h**) could still be obtained in a comparable 94% isolated yield (Scheme 3).

To gain insight into this oxidative reaction, control experiments were employed as shown in Scheme 4. Firstly, the reaction



Scheme 2 Oxidative reaction of 2-phenylacetophenone.



Scheme 3 Scale-up synthesis.



Scheme 4 Control experiments.



Scheme 5 Proposed mechanism.

was stopped after 5 hours, the oxidation product **2h** and radical adducts **4** were both observed in 66% and 30% yields respectively. When intermediate **4** was subjected to the standard reaction conditions, the corresponding product **2h** was also obtained in 91% yield. When the diphenylmethanol (**5**) was subjected to the standard reaction conditions, the desired ketone product **2h** was also obtained with 95% yield. These results indicated that this transformation might involve benzylic peroxides and/or benzylic alcohols as the reaction intermediates.

On the basis of the above-mentioned experimental results and previous reports,¹⁷ a plausible reaction mechanism was proposed in Scheme 5. First, the decomposition of TBHP generated the oxygen-based radicals, which then underwent hydrogen abstraction of substrate **A** to generate intermediate **B**. The radical intermediate **B** can either react with $^\bullet\text{OH}$ or $^\bullet\text{OO}t\text{Bu}$ to form the oxygenated intermediate **C** or **D**. The intermediate **D** either eliminated one molecule of $t\text{BuOH}$ to directly form ketone **E**, or transformed into the benzyl alcohol **C**, which then underwent further oxidation to give final aryl ketone product **E**.

Conclusions

In summary, a simple metal-free TBHP system has been identified for direct oxidation of benzylic methylene groups to the corresponding aryl ketones. The radical-based reaction pathway tolerates a large variety of benzylic C–H bonds, giving the desired product in good to excellent yields. More importantly, the methodology is amenable to challenging heterocyclic substrates, such as pyridines and imidazoles. The synthetic utility of this protocol was further showcased in the gram-scale synthesis of diphenylketone. Further studies on both reaction scope and reaction mechanism are currently under investigation in our group.

Acknowledgements

We are grateful to Fundamental Research Funds for the Central Universities in Beijing University of Chemical Technology, and the Natural Science Foundation of China (21602119, U1504208),



the financial support from He'nan Provincial Department of Science and Technology (152300410117).

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