



An environmentally benign benzylic oxidation catalyzed by hypervalent iodine intermediate in water

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Abstract

An effective and environmentally benign benzylic oxidation for transition of alkylarenes into the corresponding carbonyl compounds was reported. Alkylarenes were mixed and stirred with potassium bromide, *m*-chloroperbenzoic acid and a catalytic amount of iodobenzene in water at 60 °C for several hours, a series of the corresponding carbonyl compounds was obtained in moderate to good yields. In the reaction, iodobenzene was first oxidized by *m*-chloroperbenzoic acid into the hypervalent iodine intermediate which then reacted with potassium bromide to form the key radical initiator for the benzylic oxidation.

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Keywords: Benzylic oxidation; Hypervalent iodine intermediate; Catalytic reaction; Synthesis

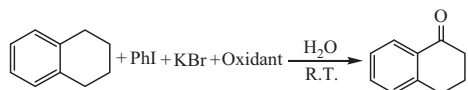
Benzylic oxidation of alkylarenes into ketones is one of the most significant and synthetically useful methods in organic chemistry. These are numerous methods for the benzylic oxidation, and the use of stoichiometric quantities of oxidants such as potassium permanganate or potassium dichromate in these reactions is the classical process [1]. During the last decades, a number of oxidation catalysts have been described [2], but most of them involve toxic metals, such as Cr, Co, Ru, Mn, Bi and Rh, and their applicability is limited [3–10]. Having low toxicity, mild reactivity and high stability, the hypervalent iodine reagents-induced benzylic oxidations are new improvement processes; however, in these reactions the stoichiometric hypervalent iodine reagents are needed and most of the reactions occur in organic solvents [11–15]. Kita group reported a new green benzylic oxidation using water as solvent in 2008, in which 3 equiv. of hypervalent iodine reagent iodosobenzene was used [16].

Recently, the catalytic utilization of hypervalent iodine reagents is increasing in importance, with the growing interest in the development of environmentally benign synthetic transformations [17–21]. In these catalytic reactions, a catalytic amount of an iodine-containing molecule together with a stoichiometric oxidant is used. The oxidant generates the hypervalent iodine reagent *in situ*, and after the oxidative transformation, the reduced iodine-containing molecule is re-oxidized. Ochiai et al. reported the α -acetoxylation of ketones with iodobenzene as catalyst and metachloroperbenzoic acid (*m*CPBA) as oxidant [22]. Kita's group demonstrated the catalytic spirocyclization of phenol derivatives using hypervalent iodine reagents as catalysts [23]. In order to extend the scope of catalytic use of hypervalent iodine reagents in organic synthesis, we have explored some reactions with catalytic hypervalent iodine

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Table 1
Optimization of the iodobenzene catalyzed oxidation of tetrahydronaphthalene.



Entry	Oxidant (equiv.)		KBr (equiv.)	Time (h)	Yield (%) ^a
1	<i>m</i> CPBA	2.0	0.1	24	28
2	Oxone [®]	2.0	0.1	24	29
3	<i>t</i> -BuOOH	2.0	0.1	24	8
4	K ₂ S ₂ O ₈	2.0	0.1	24	Trace
5	NaBO ₃ ·4H ₂ O	2.0	0.1	30	Trace
6	<i>m</i> CPBA	2.0	0.3	18	48 ^b
7	Oxone [®]	2.0	0.3	18	48 ^b
8	<i>m</i> CPBA	1.2	0.3	18	51 ^b
9	Oxone [®]	1.2	0.3	18	52 ^b

^a Determined by ¹H NMR spectroscopy.

^b Reactions were performed at 60 °C.

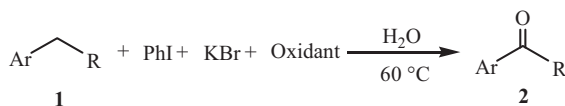
reagents generated *in situ*, and reported the α -phosphoryloxylation of ketones [24] and sulfonyloxylactonization of alkenoic acids [25]. More recently we have investigated the new environmentally benign benzylic oxidation using iodobenzene as catalyst and *m*CPBA as oxidant in the presence of potassium bromide in water, a series of the corresponding carbonyl compounds was obtained in moderate to good yields. Now we would like to report the new environmentally benign benzylic oxidation, and this catalytic process in water has never been reported before.

Firstly, tetrahydronaphthalene was chosen as the model substrate to investigate the catalytic benzylic oxidation. When 1.0 equiv. of tetrahydronaphthalene was treated with 2.0 equiv. of *m*CPBA, 0.1 equiv. of potassium bromide and iodobenzene in water at room temperature, it was found that after 24 h the reaction provided the desired product of 3,4-dihydronaphthalen-1(2H)-one in 28% yield. Prompted by the result, a series of experiments was performed to determine the suitable reaction conditions, the results are summarized in Table 1.

It is shown from Table 1 that when another oxidant Oxone[®] (KHSO₄·2KHSO₅·K₂SO₄) was used in place of *m*CPBA, the reaction gave the nearly same yield (entries 1, 2). Other oxidants, such as *t*-BuOOH, K₂S₂O₈ and NaBO₃·4H₂O were not active in the reaction (entries 3–5). It was found that the amount of KBr and reaction temperature influenced on the yield greatly. When 0.3 equiv. of KBr was added and the reaction was performed at 60 °C, the reaction yield was increased to 48% after 18 h either *m*CPBA or Oxone[®] was used as oxidant (entries 6 and 7). Due to part of product can be further oxidized into the by-product of ester by more oxidant, the amount of oxidant was also investigated and 1.2 equiv. of oxidant should be suitable to the reaction (entries 8 and 9).

Having establishing optimal conditions, the catalytic benzylic oxidation of a series of alkylarenes (1) with 1.2 equiv. of *m*CPBA or Oxone[®] and 0.3 equiv. of KBr in the presence of 0.1 equiv. of iodobenzene in water at 60 °C was investigated, and several corresponding carbonyl compounds (2) were obtained (Scheme 1), the results are summarized in Table 2.

It is notable that the cyclic and linear alkylbenzenes gave the corresponding arylketones in moderate to good yields (Table 2, entries 1–5). Both diarylmethanes **1f** and **1g** provided the products in quite different yields: the dibenzenemethane was oxidized into the ketone in excellent yield of 84%; while **1g** which had an electron-withdrawing group at benzene ring and an electron-withdrawing pyridine ring only let to the corresponding product



Scheme 1.

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