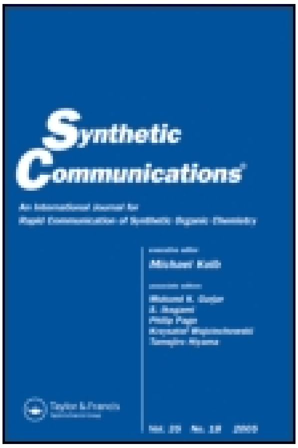

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Simple and Facile Benzylic C-H Oxidation Using (Diacetoxyiodo)benzene and Catalytic Sodium Azide

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SIMPLE AND FACILE BENZYLIC C-H OXIDATION USING (DIACETOXYIODO)BENZENE AND CATALYTIC SODIUM AZIDE

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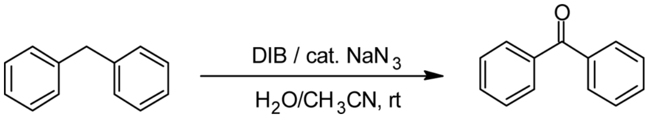
GRAPHICAL ABSTRACT



Abstract *A synthetic utility of hypervalent iodine reagent, (diacetoxyiodo)benzene, with a catalytic amount of sodium azide for oxidation of benzylic C-H to corresponding ketone compounds is described. The advantage of this protocol is characterized by mild reaction conditions and shorter reaction time to obtain moderate to good yields.*

Keywords Benzylic C-H; (diacetoxyiodo)benzene; ketones; oxidation

INTRODUCTION

Hypervalent iodine reagents have attracted increasing interest during the past decade because of their selective, mild, and ecofriendly properties as oxidizing agents in organic synthesis.[1] The relevance of this methodology stems from the fact that all the aforementioned transformations are quite fundamental in nature and can be easily applied to a multitude of synthetic strategies. Investigations from our laboratories have revealed a series of new paradigms for hypervalent iodine-mediated reactions under mild conditions.[2,3]

Benzylic oxidation is a fundamental transformation that is useful for the conversion of alkylarenes into corresponding carbonyl compounds. Generally, hypervalent iodine reagents such as bis(trifluroacetoxyiodo)benzene and 1-hydroxy-1,2-benziodoxol-3(*1H*)-one are used in combination with *tert*-butyl hydroperoxide for the benzylic C-H oxidation. In this case, first the hypervalent iodine reagent and *tert*-butyl hydroperoxide are reacted at a low temperature and bis(*tert*-butylperoxy)-iodane molecule is generated in-situ. With further increase in

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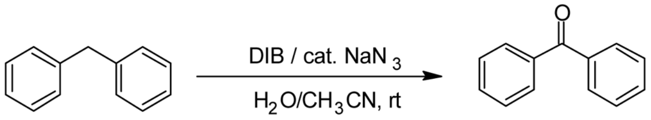


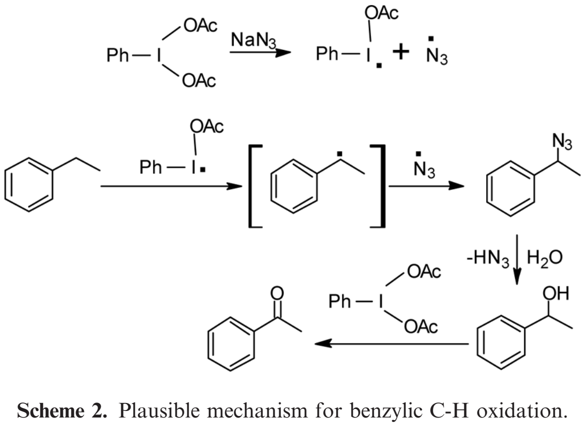
Scheme 1. Bezylic C-H oxidation using DIB and catalytic sodium azide.

reaction temperature, this bis(*tert*-butylperoxy)-iodane molecule decomposes into the *tert*-butyloxidanyl radical, which is responsible for oxidation of benzylic C-H.[4,5] Thus, all these methods require lower reaction temperature initially for in situ generation of bis(*tert*-butylperoxy)-iodane and higher temperature for oxidation of benzylic C-H, as well as tedious workup procedure and long reaction time. Therefore, a new method with mild reaction conditions is of great importance. Other than these reactions, there is only one catalytic method reported: polymeric iodosobenzene in the presence of catalytic KBr in water for benzylic oxidation.[6]

(Diacetoxyiodo)benzene (DIB) is a hypervalent iodine reagent that is readily available and frequently used in several oxidative transformations.[7,8] During the course of our studies, we found that treatment of (diacetoxyiodo)benzene with diphenylmethane in an acetonitrile/water mixture in the presence of a catalytic amount of sodium azide at room temperature resulted in the formation of diphenylmethanone (Scheme 1). It was interesting to know that in the absence of sodium azide no oxidation reaction was observed. Further solvent study indicated that dichloromethane/water and chloroform/water are also suitable solvents for this conversion.

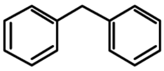
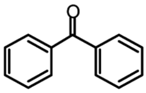
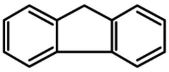
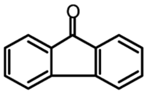
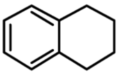
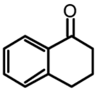
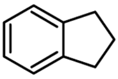
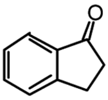
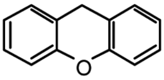
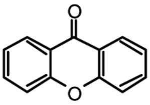
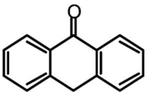
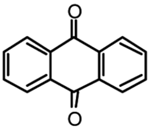
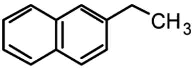
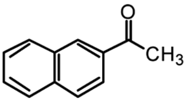
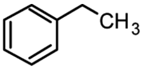
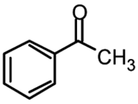
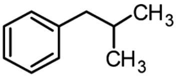
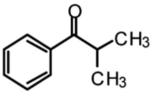
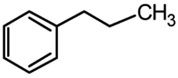
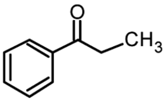
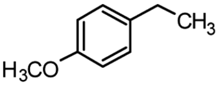
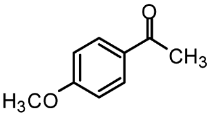
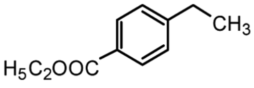
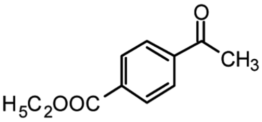
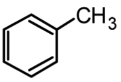
We also carried out the reaction in water, but a slower reaction rate was observed (4 h) because of heterogeneous nature of the reaction. In the case of dry acetonitrile, no reaction was observed, and thus water is required for the reaction. On the basis of these observations, we propose a plausible radical mechanism for benzylic C-H oxidation (Scheme 2)

The mechanism involves the formation of an iodanyl radical by using sodium azide. The water molecule is required to generate HN_3 and secondary alcohol, which is further oxidized into the product using another mole of (diacetoxyiodo)benzene.



Scheme 2. Plausible mechanism for benzylic C-H oxidation.

Table 1. Oxidation of benzylic C-H using (diacetoxyiodo)benzene and catalytic sodium azide[a]

Entry	Substrate	Product	Time (min)	Yield[b] (%)
1			20	85
2			20	87
3			20	85
4			20	84
5			25	80
6			25	80
7			25	85
8			30	85
9			30	84
10			30	85
11			30	85
12			30	85
13		—	120	NR[c]

[a] Reaction conditions: substrate (5.91 mmol), (diacetoxyiodo)benzene (2 equiv), and NaN_3 (0.1 equiv) in CH_3CN/H_2O (10 mL).

[b] Isolated yields after column chromatography and structures were confirmed by comparison of IR and ^1H NMR with authentic materials.

[c] No reaction.

RESULTS AND DISCUSSION

To explore the reaction scope, a variety of benzylic compounds were subjected to this reaction condition and oxidized to the corresponding ketones in moderate to good yields; the results are summarized in Table 1. It was found that five- and six-member cyclic compounds successfully undergo oxidation reaction; 9H-flurene, indan, and tetralin afforded the corresponding ketone compounds in good yields (Table 1, entries 2–4). Heterocyclic compounds such as 9H-xanthene also converted into corresponding 9H-xanthen-9-ones (Table 1, entry 5). The developed method is also applicable for the preparation of anthacene-9,10-dione (Table 1, entry 6). Further investigations indicated that linear alkylbenzenes also are suitable compounds for this transformation; 1-ethylnaphthalene, ethylbenzene, (2-methylpropyl)-benzene and propylbenzene successfully converted to corresponding ketones in a short reaction time (Table 1, entries 7–10). Under these reaction conditions, no hydrolysis of ether and ester groups was observed (Table 1, entries 11 and 12). It was interesting to know that only benzylic compounds undergo this reaction transformation, and thus no reaction was observed when toluene was subjected to these reaction conditions (Table 1, entry 13).

In conclusion, a new reaction system using trivalent iodine reagent, (diacetoxoyiodo)benzene, in combination with catalytic sodium azide has been developed that is capable of converting various benzylic C-H compounds into corresponding ketones at room temperature. The method is mild and gives moderate to good yields.

EXPERIMENTAL

Catalytic NaN_3(0.1 equiv) was added to a stirred solution of (diacetoxyiodo)-benzene (2 equiv) in CH_3CN/H_2O (10 mL) at room temperature. The reaction mixture was stirred for 2 min, followed by addition of diphenylmethane (1.0 equiv, 5.91 mmol). After completion of the reaction (thin-layer chromatography, TLC), the reaction mixture was diluted with H_2O (25 mL) and the resultant solution was extracted with CH_3Cl (2×25 mL). The combine organic layer was washed successively with 10% sodium bisulfate solution (2×20 mL), 10% sodium bicarbonate (2×15 mL), and water (2×20 mL). The organic layer was dried over anhydrous sodium sulfate and concentrated under reduced pressure to give the crude product. Pure diphenylmethanone (85%) was obtained after silica-gel column chromatography (10% EtOAc-hexane).

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