

A Mild and Efficient Oxidation of Alcohols in Water

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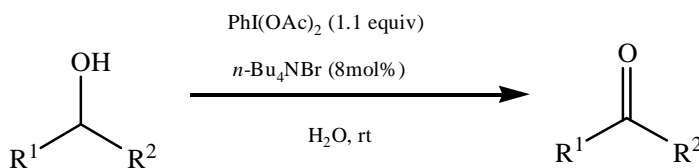
Abstract: A mild and efficient oxidation of alcohols to the corresponding carbonyl compounds using the $\text{PhI}(\text{OAc})_2$ (1.1 eq.) with $n\text{-Bu}_4\text{NBr}$ (8 mol %) in water at room temperature is described. This new procedure is very simple and affords the desired carbonyl compounds in high yields.

Keyword: Oxidation, alcohols, $n\text{-Bu}_4\text{NBr}$, $\text{PhI}(\text{OAc})_2$, water.

The oxidation of alcohols to corresponding carbonyl compounds is one of the most important functional group transformations in organic synthesis, which has received much attention over the years¹. Despite the availability of many reagents for this transformation², there still exists a need for mild and efficient methods. Hypervalent iodine(III) are now extensively used in organic synthesis³. In particular, phenyliodine(III) diacetate and phenyliodine(III) bis(trifluoroacetate) have received a great deal of attention due to their reactivities similar to that of heavy metal reagents or anodic oxidation, low toxicity, ready availability and easy to handle. The use of water as the reactions have been developed⁴. Recently, Kita *et al.*, have briefly communicated the oxidation of alcohols using iodosobenzene ($\text{PhI}=\text{O}$) (1.5 eq.) with an inorganic bromide salt, such as KBr (20 ~ 100 mol %), in water under neutral conditions⁵. On the other hand, (diacetoxyiodo) benzene [$\text{PhI}(\text{OAc})_2$], the previous substance of iodosobenzene ($\text{PhI}=\text{O}$), was found to be an effective oxidant in epoxidation of alkenes⁶.









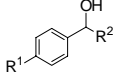
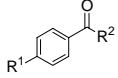








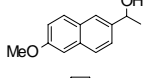
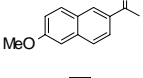




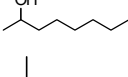
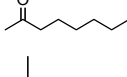
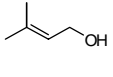
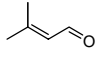
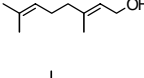
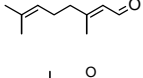
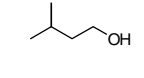
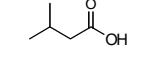
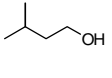
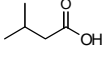
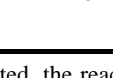
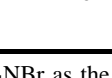
Herein, we report a mild and efficient oxidation of various alcohols such as benzylic alcohols, primary alcohols and secondary alcohols to carbonyl compounds with $\text{PhI}(\text{OAc})_2$ catalyzed by bromide salt in water at room temperature (**Scheme 1**).

Scheme 1



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Table 1 Oxidation of various alcohols with $\text{PhI}(\text{OAc})_2$ in $\text{H}_2\text{O}^{\text{a}}$

Entry	Substrate	Product	Time(h)	Yield(%)
1c			6	20.6
2d			6	24.1
3e			2	98.5
4f			2	100
5			1	100
6			2	100
	R1=Me, Br, CF3	R2=Me, C2H5		
7			2	100
8			2	100
9			2	100
10			4	13.1
11			2	100
12			1	100
13			2	100
14			1	100
15			1	100
16			4	34
17			6	47.6
18			2	49.6
19			2	100

a. Unless otherwise noted, the reaction used $n\text{-Bu}_4\text{NBr}$ as the catalyst and the reaction condition are: substrate : oxidant : catalyst = 1 : 1.1 : 0.08, room temperature. b. GC yields are average of two or more runs and base on the amount of substrate consumed. c. Free of catalyst d. $n\text{-Bu}_4\text{NCl}$ as catalyst. e. KBr as catalyst. f. $[\text{bmim}]\text{Br}$ as catalyst. g. Substrate : oxidant : catalyst=1 : 1.1 : 0.25. h. Substrate : oxidant : catalyst = 1 : 2.1 : 0.08.

As shown in **Table 1**, various types of alcohols have been successfully used. The procedure is very simple. The results of oxidation of *sec*-phenethyl alcohol catalyzed by various catalyst are summarized in entry 1 ~ 5. One can see from the results that the addition of bromide ions, such as *n*-Bu₄NBr, [bmim]Br and KBr, was found to activate PhI(OAc)₂ remarkably to give *sec*-phenethyl ketone in good yield, while *n*-Bu₄NCl did not catalyze the reaction effectively. Therefore *n*-Bu₄NBr, the most active and relative economic bromide, was chosen for further studies.

The results for the oxidation of a variety of alcohols are summarized in **Table 1**, it is clear that, in spite of chromanol (entry 10) failing to be oxidated, the reaction of benzyl alcohols to the corresponding carbonyl compounds is fast and efficient. Oxidation of most benzyl alcohols was completed within two hours and gave the corresponding ketones in good yield. Aliphatic alcohols are also viable substrates. As expected, secondary aliphatic alcohols (entry 12 ~ 14) were oxidized more quickly than primary alcohols (entry 16 ~ 19). Oxidation of primary allylic alcohols give the corresponding aldehyde cleanly. Not surprisingly, the oxidation of allylic alcohols is challenging problem (entry 15 ~ 17). The 3-methyl-2-buten-1-ol was oxidized (entry 15) successfully under the same condition. In addition, in the case of geraniol (entry 16 ~ 17), the yield cannot be enhanced greatly by increasing the catalyst and reaction time. Oxidation of primary aliphatic alcohols (entry 18 ~ 19) only gave carboxylic acid and none of the corresponding aldehyde was obtained, when 1.1 eq. PhI(OAc)₂ was used, but when using 2.1 eq. oxidant the substrate can be consumed completely within the same time (entry 19).

Typical procedure: PhI(OAc)₂ (70.8 mg, 0.22 mmol) and *n*-Bu₄NBr (5.2 mg, 0.016 mmol) were added to water (3 mL) and stirred at room temperature. 2-Octanol (260.5 mg, 0.2 mmol) was then added and stirring was continued at room temperature for 1 hour. The reaction mixture was extracted with ethyl acetate, washed with brine. The organic layers were dried over anhydrous MgSO₄. The yields were determined by gas chromatography (HP 5890II). The products were characterized by GC-MS (Agilent 6890N GC/5793 MS).

In summary, we have achieved a mild and efficient oxidation of alcohols to corresponding carbonyl compounds with the catalysts, the PhI(OAc)₂ and *n*-Bu₄NBr, in water at room temperature.

Acknowledgments

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