Bismuth Tribromide Catalyzed Oxidation of Alcohols with Aqueous Hydrogen Peroxide

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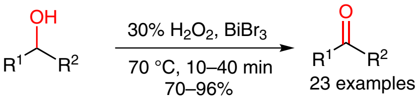

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Abstract An efficient bismuth tribromide catalyzed oxidation of various alcohols with aqueous hydrogen peroxide is described, leading to the corresponding carbonyl compounds.

Key words alcohols, catalysis, green chemistry, oxidation, hydrogen peroxide

The oxidative transformation of alcohols into the corresponding carbonyl compounds occupies an important place in the realm of synthetic organic chemistry.[1,2] Numerous methods have been developed for this conversion, and some of the conventionally used protocols involve oxidants like pyridinium chlorochromate,[3] triphenylmethylphosphonium dichromate,[4] oxone,[5] iodine,[6] $Mn(OAc)_3$/DDQ,[7] *N*-hydroxyindole/copper(I) chloride,[8] and ruthenium hydrotalcite.[9] Among others, hydrogen peroxide has attracted great attention for the oxidation of alcohols due to its eco-friendly nature and ready availability. In general, hydrogen peroxide has been utilized for the oxidation of alcohols in combination with sophisticated complexes of transition metals such as aluminum,[10] iron,[11] manganese,[12] molybdenum,[13] or tungsten.[14,15] In addition, hydrogen peroxide mediated oxidations of alcohols with HBr[16] or NaBr/AcOH[17] have been reported. However, many of them are associated with the use of exotic transition-metal complexes, long reaction times, modest isolated yields, and user-unfriendly, harsh reaction conditions which limit their practical synthetic application. Furthermore, the above-mentioned hydrogen peroxide mediated oxidation methods generally use phase-transfer catalysts in harmful volatile organic solvents which are not desirable in a healthy environment.[11] Therefore, development of an alternative hydrogen peroxide mediated oxidative protocol for alcohols with more environmentally benign and cost-effective reaction conditions is still a challenge.

Water has received much attention as a greener alternative reaction medium to toxic and volatile organic solvents for a variety of organic reactions.[18] Water can exhibit unique solvent behavior like rate acceleration[19] and enhanced selectivity[20] compared to reactions in conventional organic solvents. However, the oxidation of primary alcohols with aqueous hydrogen peroxide often provided mainly over-oxidized carboxylic acid derivatives. For instance, the oxidation of benzaldehyde in the presence of H_2O_2 and Au/TiO_2 provided benzoic acid.[21] To date, only a few examples of methods for effective hydrogen peroxide mediated oxidation of alcohols to the corresponding carbonyl compounds in organic solvent-free aqueous systems have been reported.[22,23]

Bismuth tribromide, an inexpensive, less toxic, and readily available reagent, has been used in various organic transformations such as halogen-exchange reactions,[24] cyanation of carbonyl compounds,[25] oxidation of sulfides to sulfoxides,[26] and preparation of alkyl ethers.[27] However, there is only a single example of the application of bismuth(III) complexes for the oxidation of alcohols. This method utilized bismuth(III) nitrate in combination with acidic zeolite materials in PEG 1500 for the oxidation of benzylic alcohols to aldehydes.[28]

To the best of our knowledge, the application of bismuth tribromide for the oxidation of alcohols has not been previously reported. Thus, it is highly desirable to develop a new environmentally benign method for the oxidation of alcohols to the corresponding carbonyl compounds utilizing bismuth tribromide in combination with aqueous hydrogen peroxide as an economical and greener oxidative system.

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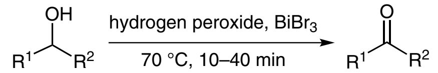
As a part of our continued efforts to develop eco-friendly oxidative procedures for alcohols, we report here a novel method for the efficient oxidation of benzylic and aliphatic alcohols by inexpensive and easily accessible bismuth tribromide and aqueous 30% hydrogen peroxide. Treatment of benzylic alcohols with 5.0 molar equivalents of hydrogen peroxide and bismuth tribromide (10 mol%) for 10–40 minutes at 70 °C provided the corresponding oxidized carbonyl compounds (Scheme 1). Initial attempts to oxidize primary benzylic alcohols in the absence of bismuth did not provide the desired benzaldehydes. Furthermore, to our surprise, replacement of bismuth tribromide by bismuth trichloride generally gave unchanged starting materials. The present reaction protocol can be applied for the oxidation of a variety of primary and secondary alcohols and the results are summarized in Table 1. Both primary and secondary benzylic alcohols were efficiently oxidized to their corresponding carbonyl compounds in high yields. In all cases of oxidation of primary benzylicalcohols, our conditions resulted in exclusive formation of aldehydes, without over-oxidized carboxylic acids being detected. However, over-oxidized carboxylic acid began to form in prolonged reaction times of more than two hours. Moreover, electrophilic bromination at the aromatic ring was not observed in all the cases tested. The position of substituents on the aromatic ring did not influence the yields of the oxidation reactions (entries 2–5). In addition, the results demonstrated that electron-donating or -withdrawing substituents on the aromatic ring of the substrates did not significantly affect the efficiency of the oxidation reactions. In general, the oxidation of secondary benzylic alcohols proceeded faster than that of primary alcohols. The protocol was also successfully applicable to the oxidation of an allylic alcohol (entry 20) or aliphatic alcohols (entries 21–23) to provide the desired products in high yields. The oxidation presumably occurred by the reaction of the alcohol with hypobromous acid, formed in situ by the reaction of bismuth tribromide and hydrogen peroxide, to give a hypobromite intermediate in line with a previously reported analogous observation of the oxidation of alcohols with NaBr–$NaBrO_3$.[29]



Scheme 1

In summary, a facile and efficient oxidation of various alcohols has been achieved in short reaction times by the reaction of aqueous 30% hydrogen peroxide with readily available bismuth tribromide.[30] This organic solvent-free method may serve as a user-friendly alternative to the existing methods for the oxidation of alcohols.

Table 1 Oxidation of Alcohols with Hydrogen Peroxide and Bismuth Tribromide

Entry	Substrate	Product	Time (min)	Yield (%)[a]
1	$PhCH_2OH$	PhCHO	30	90
2	2-$MeC_6H_4CH_2OH$	2-MeC_6H_4CHO	30	93
3	4-$MeC_6H_4CH_2OH$	4-MeC_6H_4CHO	30	92
4	2-$ClC_6H_4CH_2OH$	2-ClC_6H_4CHO	30	85
5	4-$ClC_6H_4CH_2OH$	4-ClC_6H_4CHO	30	89
6	4-$BrC_6H_4CH_2OH$	4-BrC_6H_4CHO	30	85
7	4-$MeOC_6H_4CH_2OH$	4-$MeOC_6H_4CHO$	30	72
8	4-$O_2NC_6H_4CH_2OH$	4-$O_2NC_6H_4CHO$	30	80
9	naphthalen-1-ylmethanol	1-naphthaldehyde	10	75
10	PhCH(OH)Me	PhCOMe	10	80
11	PhCH(OH)Et	PhCOEt	10	85
12	4-$MeC_6H_4CH(OH)Me$	4-MeC_6H_4COMe	20	90
13	4-$ClC_6H_4CH(OH)Me$	4-ClC_6H_4COMe	10	95
14	4-$BrC_6H_4CH(OH)Me$	4-BrC_6H_4COMe	10	95
15	4-$FC_6H_4CH(OH)Me$	4-FC_6H_4COMe	10	96
16	1-(naphthalen-2-yl)ethanol	2-acetonaphthone	10	80
17	α-tetralol	α-tetralone	10	85
18	PhCH(OH)Ph	PhCOPh	40	85
19	$PhCH(OH)CO_2Et$	$PhCOCO_2Et$	10	88
20	$PhCH=CHCH_2OH$	PhCH=CHCHO	10	75
21	cyclohexanol	cyclohexanone	10	85
22	1-nonanol	nonanal	30	72
23	2-octanol	2-octanone	10	70

[a] Isolated yield.

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(30) **General Experimental Procedure for the Oxidation of Alcohols:** To a solution of the alcohol (1.0 mmol) and hydrogen peroxide (5.0 mmol, 30% aq) was added BiBr$_3$ (10 mol%). The reaction mixture was stirred at 70 °C for 10–40 min, and the reaction mixture was extracted with dichloromethane (2 × 5 mL). The combined organic layers were washed with saturated brine (2 × 5 mL) and dried with anhydrous MgSO$_4$. After evaporation of the solvent, the residue was purified by flash column chromatography (SiO$_2$; CH$_2$Cl$_2$–hexane, 3:2) to afford the pure carbonyl compound.

4-Methylbenzaldehyde (**Table 1, entry 3**)**:** colorless oil; 111 mg (92% yield). ^{1}H NMR (300 MHz, CDCl$_3$): δ = 9.94 (s, 1 H), 7.76 (d, *J* = 8.1 Hz, 2 H), 7.32 (d, *J* = 8.1 Hz, 2 H), 2.42 (s, 3 H).

Benzophenone (Table 1, entry 18): off-white solid; 155 mg (85% yield). ^{1}H NMR (300 MHz, CDCl$_3$): δ = 7.68 (m, 4 H), 7.51–7.40 (m, 2 H), 7.39–7.29 (m, 4 H).

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