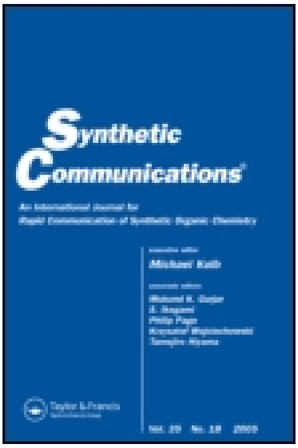

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Direct and Selective Conversion of Benzyl Bromides to Benzaldehydes with Aqueous H_2O_2 Without Catalyst

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DIRECT AND SELECTIVE CONVERSION OF BENZYL BROMIDES TO BENZALDEHYDES WITH AQUEOUS H_2O_2 WITHOUT CATALYST

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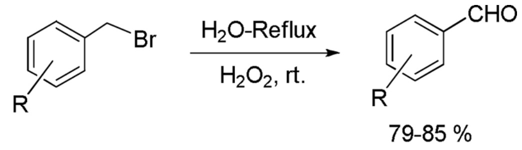
GRAPHICAL ABSTRACT



R = H, NO_2, Cl, Br, CH_3, etc.

Abstract *The facile and selective conversion of benzylic bromides to benzaldehydes using H_2O_2 as a benign oxidizing agent in an aqueous medium is described. Under these conditions, good yields of benzaldehydes were obtained.*

Keywords Benzyl bromides; hydrogen peroxide; oxidation benzaldehydes

INTRODUCTION

Organic reactions in water have received increased attention primarily because of their environmental acceptability, abundance, and low cost.[1] Water as the reaction medium is certainly the best choice in the constant search for cheaper, cleaner, and more efficient technologies for the transformations of organic molecules.[2] Moreover, water also exhibits unique reactivity and selectivity that cannot be attained in conventional organic solvents.[3]

The development of sustainable, efficient, and selective catalysts and reagents for the oxidation of alcohols to aldehydes is an important and fundamental reaction in academia and industry. During the past decade, many transition-metal-catalyzed reactions[4–8] have been uncovered for direct oxidation of benzylic alcohols to aldehydes. The scarcity of these precious metals and their high price limits their applications. The conversion of benzyl halides to benzaldehydes is the best alternate as benzyl halides are easily accessible from methyl arenes.[9] Many methods have been

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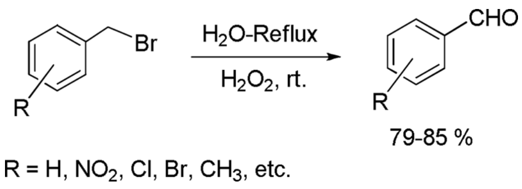


Scheme 1. Oxidation of benzyl bromides to benzaldehydes.

developed for the conversion of benzyl halides to benzaldehydes.[10] The Kornblum reaction is the most notable method for this transformation.[11] In continuation of our work on the oxidation of benzylic/secondary alcohols to corresponding carbonyl compounds,[12–14] we report here the direct conversion of benzyl bromides to benzaldehydes using H_2O_2 as a benign oxidizing agent, without any catalyst and in organic solvent-free conditions (Scheme 1).

RESULTS AND DISCUSSION

Various benzyl bromides (both electron-deficient and electron-rich) participated in this reaction, yielding the corresponding benzaldehydes in good yields (79–85%). The products are summarized in Table 1. In general, all the reactions were very neat and simple, as indicated by TLC. By refluxing benzyl bromides in water using hydrogen peroxide as a benign oxidizing agent, benzaldehydes were obtained directly. It should be noted that it is possible to oxidize selectively one group without affecting the other group in the same molecule (Table 1, entry 9). This is a unique advantage of the present method. This method does not require the use of expensive or corrosive reagents.

The reaction of benzyl bromides proceeds smoothly, independent of the nature of substituents (electron-deficient or electron-rich) present in the aromatic ring. The hydrolysis of benzyl bromides yield the corresponding benzylic alcohol and hydrobromic acid [Eq. 1]. It is known that HBr-H_2O_2 generates molecular bromine under aqueous medium [Eq. 2]. Further, in an aqueous medium, the molecular bromine is disproportionate to HBr and HOBr [Eq. 3].[15,16] The reactive species BrOH is reported to be a very mild and selective oxidizing agent for the conversion of various benzylic/secondary alcohols to aldehydes/ketones.[14] Thus, in the present system, the reactive species BrOH generated in situ will effect the oxidation of benzylic alcohols to aldehydes [Eqs. (1–3)] under mild conditions. However, the present system is not applicable for the conversion of aliphatic bromide to corresponding aldehydes because of the stability effects in the case of aliphatic bromides, unlike benzylic bromides.[17]

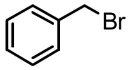
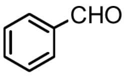
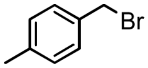
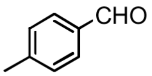
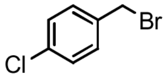
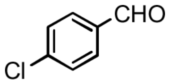
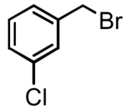
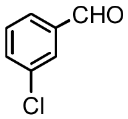
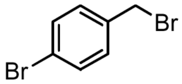
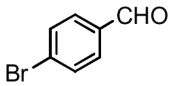
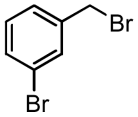
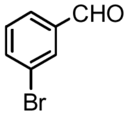
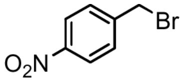
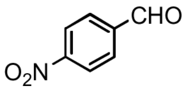
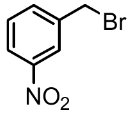
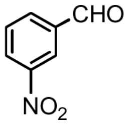
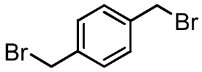
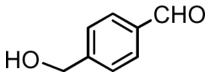
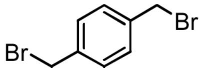
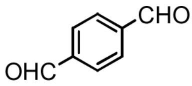
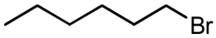
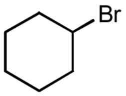
$$\mathrm{ArCH_2Br + H_2O \rightarrow ArCH_2OH + HBr} \tag{1}$$

$$\mathrm{HBr + H_2O_2 \rightarrow Br_2 + H_2O} \tag{2}$$

$$\mathrm{Br_2 + H_2O \rightarrow HOBr + HBr} \tag{3}$$

$$\mathrm{ArCH_2OH + BrOH \rightarrow ArCHO + HBr + H_2O} \tag{4}$$

Table 1. Conversion of benzyl bromides to benzaldehydes

Entry	Benzylbromide	Time (h)	Product	Yield (%)[a]
1		12		83
2		14		84
3		11		84
4		14		82
5		14		83
6		16		79
7		17		80
8		18		79
9		14		82
10		16		85
11		08	No reaction	—
12		00	No reaction	—

[a]Isolated yields.

CONCLUSIONS

In conclusion, the present method describes an efficient, selective, and environmentally friendly method for the conversion of benzylic bromides to benzaldehydes using H_2O_2 as a benign oxidizing agent in water under mild conditions. Although the present system does not work for the aliphatic bromides, it eliminated the hash reaction conditions employed in earlier procedures for these oxidations. Simple reaction conditions and excellent yields of the products make this method a facile and attractive protocol.

EXPERIMENTAL

^1H NMR spectra were recorded on a Bruker 200-MHz Fourier transform (FT)–NMR DPX-200 instrument in $CDCl_3$ with tetramethylsilane (TMS) as an internal standard, and ^{13}C NMR was determined at 50 MHz. Melting points were recorded on a Veego capillary instrument and may be uncorrected. Analytical thin-layer chromatography (TLC) was performed on Aluchrosep silica gel 60/UV_{254} purchased from Merck with ultraviolet light. Benzyl bromides were prepared according to our previously reported procedure.[9] Purification of the reaction products was carried out by column chromatography using silica gel (100–200 mesh).

General Procedure for the Conversion of Benzyl Bromides to Benzaldehydes (Benzaldehyde as Representative)

Benzyl bromide (0.5 g, 2.9 mmol) was refluxed in water (10.0 mL) for 5 h (progress of the reaction was monitored by TLC), and the reaction mixture was allowed to attain room temperature. H_2O_2 (0.4 mL, 3.5 mmol) was added slowly to this reaction mixture over 2 h, and stirring was continued for a further 5 h at room temperature. After completion of the reaction, the product was extracted with ethyl acetate (3 × 15 mL). The combined organic extracts were washed with sodium thiosulfate and dried over anhydrous sodium sulfate, and the solvent was stripped out under reduced pressure. The crude product obtained was subjected to column chromatography on silica gel to afford the pure colorless liquid (0.26 g, 2.4 mmol), benzaldehyde, in 83% yield. The spectroscopic data (IR, ^1H NMR, and ^{13}C NMR) are in good agreement with the reported values.[14] (*Caution*: All the benzyl bromides are lachrymatic, and proper care should be taken for handling.)

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