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Nitric Acid Assisted *In Situ* Generation of BrOH: A Selective Catalyst for Oxidation of Benzylic Alcohols

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Abstract

Nitric acid (15 mol%) assisted *in-situ* generated hypobromous acid catalyzed aerobic oxidation of benzyl alcohols to aldehydes under metal-free aqueous conditions is described. Nitric acid plays a dual role as "H^+" donor as well as secondary oxidant to convert bromide to a reactive species (BrOH) in presence of molecular oxygen from air.

Keywords: Benzylic alcohols; Oxidation; Nitric acid; Bromide-bromate; Benzaldehydes

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Introduction

Oxidation of alcohols to carbonyl compounds is one of the most important and fundamental functional group transformations in synthetic organic chemistry [1]. To date many excellent catalytic methods have been developed for oxidation of benzylic alcohols [2-5]. Transition metal or nitroxyl radical catalysed oxidation of alcohols to aldehydes or ketones has attracted due to the use of molecular oxygen or H_2O_2 as terminal oxidants [6-11]. Alternate to metal catalysts, halogen species (Cl, Br, and I) are frequently used for the oxidation of alcohols [12,13]. Numerous methods have been reported for the oxidation of alcohols with varying amount (2-40 mol%) of bromine or bromine based catalysts [14-22]. One of cost-effective oxidizing reagent is chlorine-gas/hypochlorite but its direct use in organic synthesis is limited due to the possibility of non-selective oxidations [23-26]. Additionally, there are useful halogen or halide derivatives such as oxy-halo compounds of bromine and iodine [27-33]. and *N*-halosuccinimides [34]. are reported for the oxidation of alcohols. Oxone has been attractive oxidant and offers several advantages such as non-toxic nature, controlled addition, stability, easy handling and ease of transport [35]. However, moleculer oxygen and aqueous H_2O_2 are greener and atom economical oxidant than oxone [36,37]. Most of the alcohol oxidation protocols were based on transition metal catalysts, these methods suffer from multiple limitations, such as requires specific conditions like inert reaction atmosphere, high temperature, toxic nature of catalyst, high price of precious metals, use of co-catalyst and reaction disposal has low environmental acceptance. On the other hand, the methods avoiding transition metal catalysts requires stoichiometric or more than stoichiometric amount of halogen sources along with other additives as well as co-catalysts [38-40].

Experimental Section

General

All commercially available chemicals and reagents were used without any further purification unless otherwise indicated. ^1H and ^{13}C NMR spectra were recorded at 200 and 125 MHz, respectively. The spectra were recorded in CDCl3 as solvent. Multiplicity was indicated as follows: s (singlet); d (doublet); t (triplet); m (multiplet); dd (doublet of doublets), sp (septet) etc. and coupling constants (J) were given in Hz. Chemical shifts are reported in ppm relative to TMS as an internal standard. The peaks around delta values of ^1H NMR (7.2), and ^{13}C NMR (77) are correspond to deuterated solvent CDCl3. Progress of the reactions was monitored by thin layer chromatography (TLC). All products were purified through column chromatography using silica gel 100-200 mesh size using hexane. All the compounds were known and spectra is matched with reported literature.

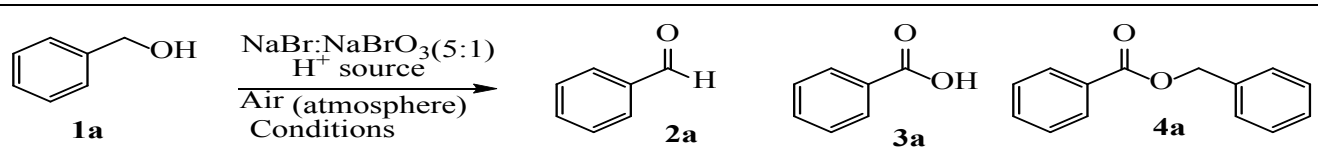
General experimental procedure for the oxidation of benly alcohol to benzaldehyde (2a)

In a 25 mL round bottomed flask, 2 mmol of benzyl alcohol **(1a),** 10 mol% of NaBr/$NaBrO_3$ 5:1 couple and 2 ml of dioxane/water (10:1) were placed. To this reaction flask 15 mol% of HNO_3 (27 mg) added. The reaction flask was placed in an oil bath at 80°C connected with condenser and continued stirring for 12 hours, after completion of the reaction mixture allowed to room temperature then extracted with 3 × 25 ml ethyl acetate and dried over anhydrous sodium sulphate. Removal of the solvent under reduced pressure, the residue left out was subjected to column chromatography on silica gel (200-400) and hexane/ethyl acetate as eluent resulted in 62% isolated yield of benzaldehyde.

Results and Discussion

In our previous communication [41,42], we disclosed an efficient and selective oxidation of benzylic/secondary alcohols to the corresponding aldehydes/ketones with a catalytic amount of bromide-bromate (10 mol %) couple as "Br" source, H_2O_2 as stoichiometric oxidant (1.2 eq.) and H^+-acid as an activator (15 mol %) at room temperature. The bromide-bromate couple in presence of acid generate BrOH/Br_2 *in-situ* which was also supported from UV-vis study [41,42]. However, there is strong need for more efficient, selective and sustainable methods that avoids the use of specific and harsh reaction conditions, stoichiometric reagents, additives, and heavy metals as catalysts for alcohol oxidations. In continuation of our interest to develop sustainable and economical processes [43-49]. We hypothesize to replace the stoichiometric use of H_2O_2 with catalytic oxidants that would be further easily reoxidized and recycled by utilising atmospheric oxygen as secondary stoichiometric oxidant without any metal catalyst. To our delight easily available nitric acid was found to be suitable for such oxidations. Our present investigation for the oxidation of alcohols to aldehydes is guided by the generation of reactive species depicted in the following chemical equations (eqns. 1-7).

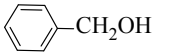
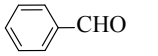
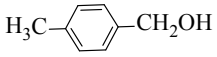
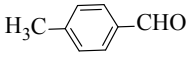
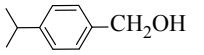
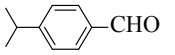
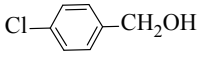
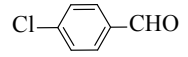
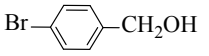
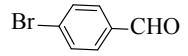
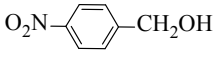
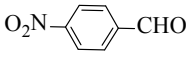
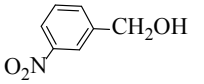
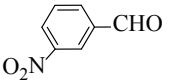
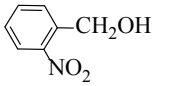
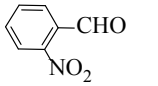
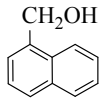
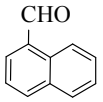
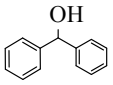
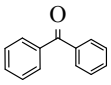
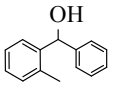
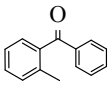
Table 1 Oxidation of benzyl alcohol to benzaldehyde[a].



Entry	Solvent (2/0.2)ml	H^+source (mol%)	Temp. (°C)	Yield(%)[b]		
				2a	3a	4a
1	Water (2)	$HN0_3$(15)	80	nr		
2	Dioxan/water	HNO_3(15)	RT	7		
3	Dioxan/water	HNO_3{15)	80	83(62)	6	1
4	Dioxan/water	$HN0_3$(10)	80	37		
5[c]	Dioxan/water	$HN0_3$(15)	80	71	2	1
6[d]	Dioxan/water	$HN0_3$(15)	80	69	2	1
7[e]	Dioxan/water	HNO_3{15)	80	66	3	
8	Dioxan/water	HC1(15)	80	17		
9	Dioxan/water	$H_2S0_4$15)	80	17		
10	Dioxan/water	CH_3COOH(15)	80	20		
11	Dioxan/water	$H_3P0i15)$	80	12		
12	DMSO/water	$HN0_3$(15)	80	2		
13	DMF/water	HNO_3{15)	80	2		
14	Ethylene glycol/water	HNO_3{15)	80	nr		
15	Ethanol/water	HNO_3{15)	80	nr		
16	THF/water	HNO_3{15)	80	20		
17	Acetone/water	HNO_3{15)	80	nr		
18	CH_3CN/water	HNO_3{15)	80	44		
19[f]	Dioxan/water	HNO_3{15)	80	16		

[a]Reaction conditions unless otherwise stated: 2 mmol of benzyl alcohol, solvent, 10 mol % of NaBr:$NaBrO_3$ (5:1) couple, acid source and in open air. [b]GC yield. [c]5 mol % NaBr:$NaBrO_3$ (5:1) couple used in the entry 5. [d]Only 10 mol% of NaBr was used in entry 6. [e]10 mol % HBr used. [f]Argon atmosphere. Yield in parenthesis is isolated yield; nr=no conversion of benzyl alcohol.

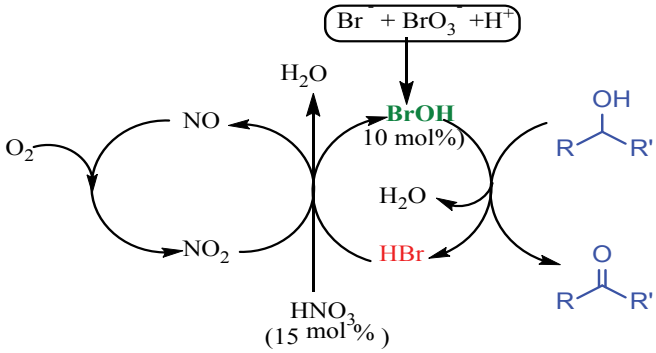
Table 2 Oxidation of benzylic alcohols to aldehydes[a].

Entry	Substrate	Product	Yield(%)[b]
1			62
2			42
3			44
4			53
5			50
6			40
7			55
8			46
9			80
10			82
11			94

[a]Reaction conditions unless otherwise stated, 2 mmol of benzyl alcohol, 10 mol % NaBr:$NaBrO_3$ (5:1) couple (w.r.t. substrate) and 15 mol % HNO_3, 80°C, open air. [b]Isolated yields

In present communication we realized that catalytic amount (15 mol %) of nitric acid plays dual role as a "H^+" donor (eqn. 1 and 2) to activate the bromide-bromate couple as well as secondary oxidant to regenerate the active bromide species (eqs. 3 and 4) at mild temperature (80°C). Further, HBr is also oxidized by NO_2 to generate BrOH/Br_2 and NO (eqn. 5). In the next step, atmospheric oxygen oxidizes NO to NO_2 species (eqn. 6) which upon water hydrolysis re-generate HNO_3 (eqn. 7). In this way the BrOH/Br_2 oxidants are effectively regenerated and reutilized for aerobic oxidation of alcohols.

To optimise suitable reaction conditions, we performed the various experiments using benzyl alcohol, bromide-bromate couple and nitric acid as model reaction parameters under various reaction conditions **(Table 1).** Initially, the reaction was conducted in water as solvent at 80°C (entry 1), and only 7% of the yield was obtained in dioxane-water mixture at room temperature with 10 mol % bromide-bromate couple as source of Br_2/BrOH, nitric acid (15 mol %) as a proton "H^+" source (entry 2). It was observed that the reaction has considerable dependence on the solvent, temperature and amount of catalyst **(Table 1,** entry 3). When the concentration of nitric acid was decreased, the yield of **2a** was dropped to 37% **(Table 1,** entry 4).



Scheme 1 Proposed mechanism for the 'Br' catalysed oxidation of alcohols.

While decreasing the total bromide concentration to 5 mol% from 15 mol%, yield was also decreased **(Table 1,** entry 5). Performing the reaction either with NaBr or HBr alone (without bromate) the oxidation was not efficient **(Table 1,** entries 6 and 7). The reaction was not effective with other acids (HCl, H_2SO_4, CH_3CO_2H, H_3PO_4) and different solvents screened **(Table 1,** entries 8-18). Nitric acid has been largely studied as an oxidizing agent either in concentrated acid as solvent media [50-52]. Oxidation reaction under argon atmosphere was also not successful. Therefore, these parameters **(Table 1,** entry 2) were set as optimum for the further oxidation of benzylic alcohols to aldehydes **(Table 2).**

The electronic effect and substitution pattern of substituents on the phenyl ring of benzyl alcohol has profound effect on the reaction rates and product yield **(Table 2).** In general, electronic releasing alkyl group (entry 2 and 3) as well as mild electronic withdrawing chloro and bromo (entries 4 and 5) derivative at *para* position gave moderate to good yields of corresponding aldehydes (42-53%). Highly electron withdrawing nitro groups were react slowly and leads to moderate to good yields (entries 6-8). 1-Napthalene methanol was also converted to 1-naphthaldehyde in 80% yield (entry 9). Noteworthy to mention that, secondary alcohols like diphenylmethonol and phenyl(o-tolyl) methanol are smoothly underwent to oxidation and afforded the corresponding ketones in 82% and 94% yields (entry 10 and 11). This might be due to benzylic effects of two benzene rings to stabilizes a reaction intermediates at transition states.

Mechanism

Based on experimental observations and literature reports [12], we proposed a probable mechanism for the present transformation **(Scheme 1).** The bromide-bromate and acid (H^+) generates bromine *in-situ* which under aqueous conditions disproportionate to HBr and BrOH. BrOH is revealed to be a mild and selective oxidizing agent for a number of organic substrates [11,12]. BrOH is the primary oxidant and oxidizes alcohol to aldehyde with the elimination of HBr **(Scheme 1).** The eliminated HBr is oxidized by HNO_3 to regenerate BrOH under aqueous conditions as predicted in eqs. 1-7. However, it should be noted that HNO_3 and O_2 (atmosphere) are necessary as secondary oxidants to complete the catalytic cycle [50-52].

Conclusion

In conclusion, we have demonstrated a simple, economical and sustainable route for selective oxidation of alcohol to corresponding aldehydes and ketones under mild reaction conditions. The yields obtained were moderate to good, compared to known oxidation systems, the present protocol is more sustainable. As both the bromide/bromate couple ("Br") and HNO_3 are inexpensive, easily available even in a undergraduate chemical laboratory. In addition, the use of atmosphere oxygen as co-oxidant makes the entire process attractive from green chemistry point of view.

Acknowledgements

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