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Efficient Oxidation of Benzylic Alcohols with Sodium Perborate in Aqueous Polyethylene Glycol

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The oxidation of alcohols to the corresponding carbonyl compounds is very important transformations in organic chemistry. In general, the oxidation of benzylic alcohols has been achieved using toxic transition metal containing oxidants which include chromium reagents(VI),[1] transition metal nitrates,[2] cobalt(II) complexes,[3] methyltrioxorhenium,[4] dinuclear iron complexes,[5] zirconium hydroxide chromate,[6] Pd with chlorobenzene,[7] and vanadium phosphorus oxides.[8] However, in this eco-conscious era, development of green oxidative methodologies has become a prime area of research interest. In this context, sodium perborate (SPB) is a desirable green oxidant due to its easy availability, high oxygen content and formation of water as ultimate byproduct.[9] To date, SPB has been employed as a powerful and selective oxidant that mediates a variety of transformations such as oxidation of anilines,[10] Baeyer-Villiger oxidation of ketones[11] and the bromination of alkenes.[12] However, the SPB mediated oxidation of benzylic alcohols was often reluctant to undergo and scanty examples are reported in the literature. For instance, oxidation reaction of benzylic alcohols with SPB provided corresponding carbonyl compounds in the presence of chromium(VI) oxide and methyltridecylammonium chloride.[13] In this protocol, long reaction times and low yields in the cases of secondary benzylic alcohols reduces its further practical applicability. More recently oxidation of benzylic alcohols to the corresponding ketones has been reported employing SPB and HBr in glacial acetic acid.[14] However, this protocol is only effective for the oxidation of secondary benzylic alcohol derivatives. Therefore, it is highly desirable to develop general oxidative method effective for both primary and secondary benzylic alcohols using SPB.

In recent years, polyethylene glycols (PEG) and its derivatives have been received a great deal of attention as greener alternative to the volatile organic solvents due to their environmentally benign characters such as low flammability, thermal stability, cheap prices and reduced toxicity.[15,16]

Herein, we wish to describe a novel environmentally benign and effective method for the oxidation of benzylic alcohols employing SPB in PEG solution. Efficient oxidation of primary and secondary benzylic alcohols to the corresponding aldehydes and ketones has been carried out by using mixture of sodium perborate, potassium bromide, and sulfuric acid in aqueous PEG-200. Oxidation took place smoothly when the mixture of benzylic alcohol, SPB (2.0 equiv.), potassium bromide (1.0 equiv.), and sulfuric acid (1.0 equiv.) was heated in PEG-200/H_2O (v/v, 4:1) at 80 °C for 1.5-2 h, giving the corresponding carbonyl compound in high yields. Our results for the oxidation of various benzylic alcohols are summarized in Table 1. Under present reaction conditions, both primary and secondary benzylic alcohols were oxidized smoothly to the corresponding aldehydes and ketones in good to excellent yields. The protocol is tolerant to electron-withdrawing and electron donating substituents. The only exception was found for the oxidation of a benzylic alcohol with powerful electron-withdrawing nitro substituent, the corresponding product formed somewhat lowered yield (entry **7**). It should be noted that in cases of primary benzylic alcohols over-oxidation of benzaldehydes was not detected under present reaction conditions. When the reactions were carried out in the absence of sulfuric acid only trace amounts of products were obtained. The influences of ratio of mixed solvent PEG-200/H_2O on reaction activity, we found that the lower or higher ratio of PEG/H_2O (v/v, 4:1)

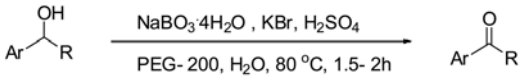

Table 1. Oxidation of benzylic alcohols with $NaBO_3$-KBr-H_2SO_4

Entry	Substrate	Product	Yield (%)[a]
1	$PhCH_2OH$	PhCHO (**1a**)	90
2	4-$MeC_6H_4CH_2OH$	4-MeC_6H_4CHO (**2a**)	85
3	4-$BrC_6H_4CH_2OH$	4-BrC_6H_4CHO (**3a**)	94
4	4-$ClC_6H_4CH_2OH$	4-ClC_6H_4CHO (**4a**)	92
5	4-$FC_6H_4CH_2OH$	4-FC_6H_4CHO (**5a**)	80
6	4-$CF_3C_6H_4CH_2OH$	4-$CF_3C_6H_4CHO$ (**6a**)	77
7	4-$NO_2C_6H_4CH_2OH$	4-$NO_2C_6H_4CHO$ (**7a**)	71
8	1-Naphtalenemethanol	1-Naphthaldehyde (**8a**)	96
9	$PhCH(OH)CH_3$	$PhCOCH_3$ (**9a**)	82
10	4-$MeC_6H_4CH(OH)CH_3$	4-$MeC_6H_4COCH_3$ (**10a**)	82
11	4-$BrC_6H_4CH(OH)CH_3$	4-$BrC_6H_4COCH_3$ (**11a**)	98
12	4-$FC_6H_4CH(OH)CH_3$	4-$FC_6H_4COCH_3$ (**12a**)	87
13	$PhCH(OH)CH_2CH_3$	$PhCOCH_2CH_3$ (**13a**)	91
14	PhCH(OH)Ph	PhCOPh (**14a**)	91
15	α-Tetralol	α-Tetralone (**15a**)	91

[a]All yields refer to pure isolated products.

was unfavorable to the reaction system. It is presumed that the active species that oxidizes the alcohols would be hypobromous acid (HOBr) in analogous with reported methods involving generation of hydrogen peroxide by treatment of sodium perborate with silica sulfuric acid.[17]

In conclusion, we report a new efficient and environmentally friendly protocol for oxidation of benzylic alcohols to corresponding carbonyl compounds with the reagent combination of SPB, KBr and sulfuric acid in aqueous PEG-200.

Experimental Section

All the benzylic alcohols and PEG-200 were purchased from Aldrich and used as received. Merck silica gel 60 (230-400 mesh) was used for flash column chromatography. All ^{1}H NMR spectra were recorded on a Varian Gemini 2000 (300 MHz) using $CDCl_3$ and TMS as solvent and respectively. All products were known and characterized by comparing their ^{1}H NMR spectra with those of reported literature data.

General Procedure. To a stirred solution of benzylic alcohol (1.0 mmol) in 2.5 mL PEG-200/H_2O (4:1) was added sodium perborate (2.0 mmol), potassium bromide (1.0 mmol) and sulfuric acid (1.0 mmol). The reaction mixture was stirred at 80 °C for 1.5 h and the reaction monitored by TLC for the complete consumption of the benzylic alcohol. The solution was cooled to room temperature and the product is extracted into diethyl ether (2 × 20 mL), washed with water and dried over $MgSO_4$. After removal of the solvent under reduced pressure, the crude product was purified by flash chromatography (dichloromethane/*n*-hexane = 2:1) to yield the desired carbonyl compound.

Benzaldehyde (1a)[18]**:** ^{1}H NMR (300 MHz, $CDCl_3$) δ 11.02 (s, 1H), 8.87 (dt, *J* = 7.7, 17.7, 2H), 8.74-8.40 (m, 3H).

4-Methylbenzaldehyde (2a)[19]**:** ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.94 (s, 1H), 7.76 (d, *J* = 8.1, 2H), 7.32 (d, *J* = 8.1, 2H), 2.42 (s, 3H).

4-Bromobenzaldehyde (3a)[20]**:** ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.97 (s, 1H), 7.75 (d, *J* = 8.5, 2H), 7.67 (d, *J* = 8.5, 2H).

4-Chlorobenzaldehyde (4a)[21]**:** ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.99 (s, 1H), 7.83 (d, *J* = 8.7, 2H), 7.51 (d, *J* = 8.3, 2H).

4-Fluorobenzaldehyde (5a)[22]**:** ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.97 (s, 1H), 7.97-7.86 (m, 2H), 7.28-7.15 (m, 2H).

4-Trifluorobenzaldehyde (6a)[23]**:** ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.11 (s, 1H), 8.02 (d, *J* = 8.0, 2H), 7.82 (d, *J* = 8.0, 2H).

4-Nitrobenzaldehyde (7a)[18]**:** ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.17 (s, 1H), 8.41 (d, *J* = 8.6, 2H), 8.09 (d, *J* = 8.9, 2H).

1-Naphthaldehyde (8a)[24]**:** ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.33 (s, 1H), 9.25-9.16 (m, 1H), 8.01 (d, *J* = 8.2, 1H), 7.92-7.79 (m, 3H), 7.64 (ddd, *J* = 1.4, 6.8, 8.5, 2H), 7.54 (ddd, *J* = 2.9, 4.2, 8.1, 2H).

Acetophenone (9a)[18]**:** ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.99-7.91 (m, 2H), 7.60-7.39 (m, 3H), 2.60 (s, 3H).

1-*p*-Tolylethanone (10a)[25]**:** ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.1, 2H), 7.24 (d, *J* = 8.1, 2H), 2.56 (s, 3H), 2.39 (s, 3H).

1-(4-Bromophenyl)ethanone (11a)[21]**:** ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.7, 2H), 7.45 (d, *J* = 8.7, 2H), 2.46 (s, 3H).

1-(4-Fluorophenyl)ethanone (12a)[23]**:** ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.87 (dd, *J* = 5.4, 9.0, 2H), 7.01 (dd, *J* = 8.5, 9.0, 2H), 2.47 (s, 3H).

Propiophenone (13a)[18]**:** ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.95 (dd, *J* = 1.4, 8.4, 2H), 7.64-7.28 (m, 3H), 2.97 (q, *J* = 7.2, 2H), 1.21 (t, *J* = 7.2, 3H).

Benzophenone (14a)[18]**:** ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.68 (dd, *J* = 1.3, 8.3, 4H), 7.51-7.40 (m, 2H), 7.39-7.29 (m, 4H).

α-Tetralone (15a)[26]**:** ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.03 (dd, *J* = 1.2, 7.8, 1H), 7.46 (td, *J* = 1.4, 7.4, 1H), 7.37-7.19 (m, 2H), 3.09-2.88 (m, 2H), 2.77-2.55 (m, 2H), 2.13 (dd, *J* = 6.5, 12.7, 2H).

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