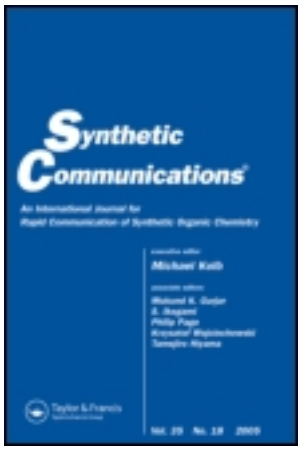

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Bon-Suk Koo [a] , Chang Keun Lee [a] & Kee-Jung Lee [b]

[a] Department of Industrial Chemistry, Hanyang University, Seoul, 133-791, Korea

[b] Department of Industrial Chemistry, Hanyang University, Seoul, 133-791, Korea

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OXIDATION OF BENZYL ALCOHOLS WITH OXONE® AND SODIUM BROMIDE

Bon-Suk Koo, Chang Keun Lee, and Kee-Jung Lee*

Department of Industrial Chemistry,
Hanyang University, Seoul 133-791, Korea

ABSTRACT

Reaction of benzyl alcohols with Oxone® and sodium bromide in aqueous acetonitrile gave the corresponding benzaldehydes in excellent yields. However, electron-rich benzyl alcohols afforded ring bromination products via bromodecarbonylation of the resulting benzaldehydes.

Key Words: Oxidation; Benzyl alcohols; Oxone®; Sodium bromide

The selective oxidation of benzylic alcohols to benzaldehydes is a transformation of considerable importance in organic synthesis. Whilst numerous reagents have been developed to effect this process, many of them use greater than stoichiometric quantities of toxic heavy metals or co-oxidants which severely handicap their applicability to large scale industrial processes.[1,2] Also, the oxidation of organic compounds by hypohalite salts or halogen is well known method in organic synthesis.[3] Especially, oxidation of primary alcohols to aldehydes with hydrogen peroxide using methyltrioxorhenium and bromide ions as cocatalysts,[4] and with oxoammonium salt and bromide ions[5] have been described.

*Corresponding author. E-mail: leekj@hanyang.ac.kr

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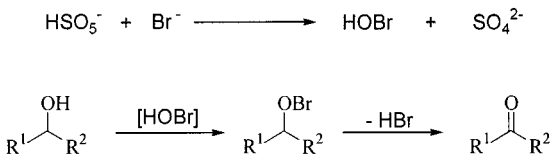
Recent reports have dealt with the use of a triple salt of potassium peroxymonosulfate, potassium hydrogen sulfate, and potassium sulfate, which is commercially available as Oxone® ($2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$), can be used for the oxidation of alkenes,[6] arenes,[7] amines,[8] imine,[9] sulfides,[10] selenides,[11] α-amino acids,[12] and acetals.[13] Also, there are reports in the literature, where Oxone® is a useful oxidation reagent of alcohols and aldehydes. Examples include the conversions of 2-propanol to acetone,[6] ethanol to ethyl acetate,[6] and benzaldehyde to benzoic acid.[6,14] Another example is the oxidation of secondary alcohols to ketones in the presence of wet-aluminium oxide in aprotic solvents.[15] Also, Bolm and co-workers have demonstrated that the combination of TEMPO/Oxone®/Bu_4NBr is an effective system for the oxidation of alcohols to aldehydes and ketones, including benzylic ones.[16] Moreover, the use of Oxone® and aqueous sodium halides was conducted as a convenient halogenating reagent to achieve oxidation of α,β-enones,[17] bromination of pyrimidines,[18] and halogenation of toluene.[6]

In previous paper, we have shown that sodium bromide combined with Oxone® serves as effective bromodecarboxylation reagent of various cinnamic acids[19] and halogenation of aromatic methyl ketones.[20] In the course of our study to extend the scope of the Oxone®/NaBr reagent in organic synthesis, we have found that this reagent facilitates the oxidation of benzylic alcohols to benzaldehydes satisfactorily.

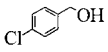
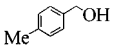
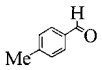
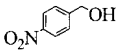
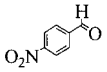
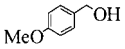
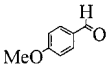
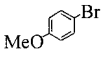
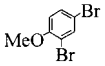
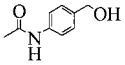
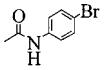
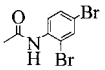
Optimization of the reaction conditions revealed that simple stirring a solution of benzyl alcohol (1 equivalent), Oxone® (1 equivalent) and sodium bromide (2 equivalent) in a 1 : 1 mixture of CH_3CN/H_2O effected the formation of benzaldehyde in 87% isolated yield within 3 h. However, in the absence of sodium bromide, the reaction did not proceed at all in 24 h at r.t. Further studies showed that this oxidation method could be applied to a wide range of benzylic alcohols and representative primary and secondary alcohols as shown in Table 1. They are all known compounds and are identified by their IR, ^1H NMR and mass spectral data.

A plausible mechanism of the oxidation is shown in Scheme 1 based on literatures. The oxidation of bromide ion by peroxymonosulfate ion would



Scheme 1.

Table 1. Oxidation of Alcohols with Oxone® and NaBr

Entry	Substrate	Time (h)	Product	No.	Yield (%)[a]
1		3		**1**	87
2		2		**2**	93
3		3		**3**	96
4		24		**4**	20[b]
5		1		**5a**	22
				**5b**	44
				**5c**	14
6		1		**6a**	63
				**6b**	20
7		3		**7**	99
8		0.5		**8**	99
9		1		**9**	91
10		0.5		**10a**	80
				**10b**	17

[a]Yields are based on isolated products, characterized by IR, ^{1}H NMR and GC-MS spectra.
[b]65% alcohol was recovered.

give the hypobromous acid[16,21] and subsequent oxidation of alcohols affords aldehydes and ketones.

The presence of electron-donating groups in the aromatic ring has little influence on the oxidation rates but these are markedly lowered by introducing a strong electron-acceptor group. Thus, *p*-nitrobenzyl alcohol was oxidized to aldehyde in only 20% yield over 24 h. Also, the reaction was unsuccessful for electron-rich arene such as *p*-methoxybenzyl alcohol, which presumably suffered complications due to competing bromodecarbonylation of the resulting *p*-anisaldehyde which was accompanied by the formation of 4-bromoanisole (44%) and 2,4-dibromoanisole (14%).[22] Similarly, *p*-acetamidobenzyl alcohol gave bromodecarbonylation products, 4-bromoacetanilide (63%) and 2,4-dibromoacetanilide (20%).[22] In the oxidation of 1-phenyl-1,2-ethanediol, the secondary benzylic alcoholic function was oxidized with high selectivity to form 2-hydroxyacetophenone in 99% yield. The oxidation of secondary alcohols afforded the corresponding ketones in excellent yields. But, primary alcohol such as 1-pentanol was converted mainly into the dimeric ester, pentyl valerate, presumably via hemiacetal intermediate.[23]

In conclusion, we developed a simple oxidation method of benzyl alcohols to benzaldehydes with Oxone®/NaBr in aqueous acetonitrile under the mild conditions. This method provides an alternative, facile preparation of benzaldehydes, since Oxone® and sodium bromide are cheap, nontoxic, stable, and easy to handle.

EXPERIMENTAL

Melting points were determined in open capillaries with an Electrothermal melting point apparatus and are uncorrected. Progress of reactions were followed by TLC using silica gel with fluorescent indicator coated on aluminium sheets. Infrared spectra were recorded on a Nicolet Magna 550 FTIR spectrometer and ^{1}H NMR spectra were measured on a Varian Gemini 300 spectrometer in $CDCl_3$ using TMS as an internal standard. Mass spectra were obtained on a ThermoQuest Polaris Q mass spectrometer operating at 70 eV.

General Procedure for the Oxidation of Alcohols with Oxone® and Sodium Bromide

To a stirred solutions of alcohols (3 mmol) in aqueous CH_3CN (30 mL, 1 : 1 by volume) was added NaBr (0.62 g, 6 mmol) and Oxone® (1.84 g,

3 mmol). Reactions were continuously monitored by thin-layer chromatography and stirred at r.t. for the time indicated in Table 1. The reaction mixture was quenched with aqueous sodium thiosulfate, and extracted with ether (3×30 mL). The combined organic layers were washed with water, dried over anhydrous $MgSO_4$, filtered, and concentrated in vacuo. The residue was chromatographed on a silica gel column and eluted with hexane–EtOAc 10 : 1 to give the products (Table 1).

Analytical Data for the Products

1: Liquid (Lit.[24] b.p. 178°C). IR (neat) cm^{-1}: 1701, 1600, 1460, 1312, 1204, 827, 749; ^1H NMR δ 7.45–7.67 (m, 3H), 7.87–7.90 (m, 2H), 10.02 (s, 1H); MS m/z (rel. intensity) 106 (M^+, 34), 105 (74), 77 (100), 51 (22).

2: M.p. 47–49°C (Lit.[24] 47.5°C). IR (KBr) cm^{-1}: 1697, 1576, 1479, 1386, 1204, 1013, 811, 539, 477; ^1H NMR δ 7.53 (d, $J = 8.5$ Hz, 2H), 7.83 (d, $J = 8.5$ Hz, 2H), 9.99 (s, 1H); MS m/z (rel. intensity) 142 (M^+, 17), 141 (58), 140 (M^+, 46), 139 (100), 113 (7), 111 (19), 77 (6), 75 (13).

3: Liquid (Lit.[24] b.p. 204–205°C). IR (neat) cm^{-1}: 1701, 1607, 1386, 1308, 1207, 1169, 847, 808; ^1H NMR δ 2.43 (s, 3H), 7.33 (d, $J = 7.9$ Hz, 2H), 7.78 (d, $J = 7.9$ Hz, 2H), 9.97 (s, 1H); MS m/z (rel. intensity) 120 (M^+, 40), 119 (100), 91 (72), 65 (28).

4: M.p. 103–105°C (Lit.[24] 106°C). IR (KBr) cm^{-1}: 1712, 1607, 1538, 1344, 1293, 1196, 854, 819, 738; ^1H NMR δ 8.08 (d, $J = 8.5$ Hz, 2H), 8.41 (d, $J = 8.5$ Hz, 2H), 10.17 (s, 1H); MS m/z (rel. intensity) 151 (M^+, 44), 150 (100), 77 (13), 51 (16).

5a: Liquid (Lit.[24] b.p. 249.5°C). IR (neat) cm^{-1}: 1685, 1600, 1507, 1312, 1262, 1161, 1025, 834; ^1H NMR δ 3.90 (s, 3H), 7.01 (d, $J = 8.5$ Hz, 2H), 7.85 (d, $J = 8.5$ Hz, 2H), 9.90 (s, 1H); MS m/z (rel. intensity) 136 (M^+, 60), 135 (100), 107 (20), 92 (9), 77 (42), 63 (14).

5b: Liquid (Lit.[24] b.p. 215°C). IR (neat) cm^{-1}: 1577, 1487, 1289, 1239, 1172, 1033, 823; ^1H NMR δ 3.77 (s, 3H), 6.78 (d, $J = 8.9$ Hz, 2H), 7.37 (d, $J = 8.9$ Hz, 2H); MS m/z (rel. intensity) 188 (M^+, 98), 186 (M^+, 100), 173 (31), 171 (30), 145 (23), 143 (26), 77 (31), 63 (47).

5c: M.p. 61–62°C (Lit.[25] 61–63°C). IR (KBr) cm^{-1}: 1576, 1475, 1378, 1263, 1052, 807, 679, 617; ^1H NMR δ 3.87 (s, 3H), 6.77 (d, $J = 8.8$ Hz, 1H), 7.37 (dd, $J = 8.8$, 2.3 Hz, 1H), 7.66 (d, $J = 2.3$ Hz, 1H); MS m/z (rel. intensity) 268 (M^+, 35), 266 (M^+, 75), 264 (M^+, 42), 253 (9), 251 (18), 249 (20), 225 (16), 223 (35), 221 (16), 172 (15), 170 (14), 63 (100).

6a: M.p. 165–167°C (Lit.[24] 168°C). IR (KBr) cm^{-1}: 3293, 1677, 1603, 1526, 1483, 1394, 1305, 1254, 1013, 823, 737, 504; ^1H NMR δ 2.04 (s, 3H),

7.47 (d, $J = 8.9$ Hz, 2H), 7.56 (d, $J = 8.9$ Hz, 2H), 10.07 (s, 1H); MS m/z (rel. intensity) 215 (M^+, 43), 213 (M^+, 43), 173 (96), 171 (100), 92 (96), 65 (41).

6b: M.p. 142–143°C (Lit.[26] 144.7°C). IR (KBr) cm^{-1}: 3289, 1658, 1572, 1522, 1460, 1367, 1293, 1040, 831, 602, 547; ^1H NMR δ 2.24 (s, 3H), 7.42 (dd, $J = 8.9$, 2.1 Hz, 1H), 7.57 (s, 1H), 7.68 (d, $J = 2.1$ Hz, 1H), 8.26 (d, $J = 8.9$ Hz, 1H); MS m/z (rel. intensity) 295 (M^+, 12), 293 (M^+, 20), 291 (M^+, 10), 253 (47), 251 (100), 249 (54), 214 (70), 212 (75), 172 (31), 170 (37), 91 (36), 90 (69), 63 (44).

7: M.p. 79–81°C (petroleum ether) (Lit.[24] 90°C). IR (KBr) cm^{-1}: 3421, 1689, 1600, 1456, 1409, 1301, 1231, 1106, 970, 761, 683; ^1H NMR δ 3.51 (t, $J = 4.6$ Hz, 1H), 4.89 (d, $J = 4.6$ Hz, 2H), 7.49–7.67 (m, 3H), 7.92–7.95 (m, 2H); MS m/z (rel. intensity) 136 (M^+, 1), 105 (77), 77 (100), 51 (17).

8: Liquid (Lit.[24] b.p. 202.6°C). IR (neat) cm^{-1}: 1681, 1596, 1448, 1359, 1262, 951, 765, 687; ^1H NMR δ 2.60 (s, 3H), 7.43–7.59 (m, 3H), 7.94–7.98 (m, 2H); MS m/z (rel. intensity) 120 (M^+, 16), 105 (100), 77 (23), 51 (9).

9: Liquid (Lit.[24] b.p. 155.6°C). IR (neat) cm^{-1}: 2939, 1712, 1452, 1304, 1223, 1118, 904; ^1H NMR δ 1.73 (m, 2H), 1.85 (m, 4H), 2.34 (dd, $J = 7.0$, 6.4 Hz, 4H); MS m/z (rel. intensity) 98 (M^+, 67), 80 (12), 69 (26), 55 (100), 42 (20), 41 (24).

10a: Liquid (Lit.[24] b.p. 203.7°C). IR (neat) cm^{-1}: 1732, 1648, 1619, 1262, 1180, 1106; ^1H NMR δ 0.91 (t, $J = 6.7$ Hz, 3H), 0.92 (t, $J = 7.3$ Hz, 3H), 1.35 (m, 6H), 1.61 (m, 4H), 2.30 (t, $J = 7.3$ Hz, 2H), 4.06 (t, $J = 6.7$ Hz, 2H); MS m/z (rel. intensity) 173 ($M^+ + 1$, 64), 172 (M^+, 3), 103 (100), 85 (70), 75 (33), 70 (86), 57 (80), 55 (79).

10b: Liquid (Lit.[24] b.p. 186°C). IR (neat) cm^{-1}: 2959, 2675, 1712, 1472, 1421, 1277, 1215, 943; ^1H NMR δ 0.93 (t, $J = 7.3$ Hz, 3H), 1.37 (sextet, $J = 7.6$ Hz, 2H), 1.63 (quintet, $J = 7.6$ Hz, 2H), 2.35 (t, $J = 7.6$ Hz, 2H); MS m/z (rel. intensity) 87 (2), 73 (28), 60 (100), 55 (13), no M^+.

ACKNOWLEDGMENTS

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