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ORIGINAL PAPER

$NaBrO_3$/bmim[HSO_4]: a versatile system for the selective oxidation of 1,2-diols, α-hydroxyketones, and alcohols

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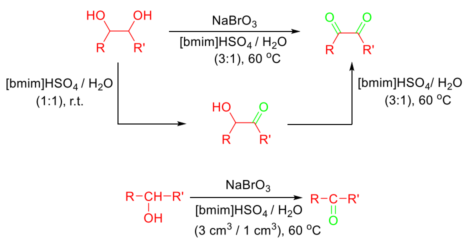
Abstract Sodium bromate with bmim[HSO_4] has been found to be an excellent oxidizing agent in aqueous medium. $NaBrO_3$:bmim[HSO_4] oxidized 1,2-diols, α-hydroxyketones, and alcohols to the corresponding carbonyl compounds in excellent yields. This method offers advantages such as low cost reagents, aqueous reaction conditions, moderate temperatures and short reaction times and hence environmentally benign reaction. Moreover, the ionic liquid bmim[HSO_4] could be recycled for at least three times without loss of significant activity.

Graphical abstract



Keywords Oxidation · Alcohols · Green chemistry · Sodium bromate · Ionic liquid

Introduction

Oxidation reactions are an important component of organic synthesis [1]. Selective oxidation of alcohols to corresponding carbonyl compounds has been reported by variety of reagents invariably in organic solvents [2–5]. In continuation of our ongoing efforts for developing inexpensive and efficient reagents for functional group transformations [6–9], we decided to investigate the potential and selectivity of sodium bromate, as an oxidizing agent. Sodium bromate is capable of multi-electron transfer and is normally used in conjunction with acidic co-reactants such as $NaHSO_3$ [10], HBr [11], ceric(IV) ammonium nitrate [12], H_2SO_4 [13], $KHSO_4$ [14], Bu_4NHSO_4 [15], $Mg(HSO_4)$ [16], silica sulfuric acid [17], and cation exchange resin [18].

Ionic liquids offer a variety of advantages over conventional solvents and are green alternatives [19, 20]. Recently, there has been lot of interest in acidic ionic liquids which serve the dual purpose of catalysis and solvent [21, 22]. Therefore, we believed that sodium bromate could be used as an oxidant in acidic ionic liquid which could act as a co-reactant and a green solvent. Furthermore, the oxidations [23, 24] using ionic liquids are highly efficient as ionic liquids are easily separable, and recyclable which makes the process more economic. We have explored the versatility of inexpensive sodium bromate in presence of acidic ionic liquid, i.e. bmim[HSO_4] as an efficient oxidation system.

Results and discussion

In this paper, we report a new, convenient, and simple procedure for the selective oxidation of 1,2-diols to α-hydroxyketones or 1,2-diketones, α-hydroxyketones to 1,2-

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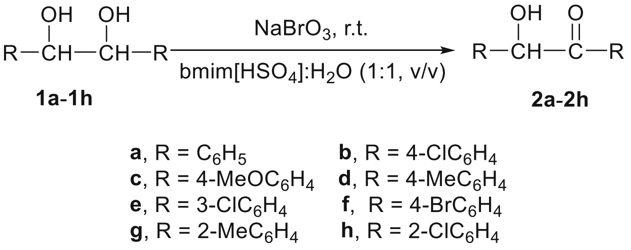
diketones and alcohols to corresponding carbonyl compounds with sodium bromate in the presence of bmim[HSO_4] which acts as a green solvent as well as the co-catalyst.

Hydrobenzoin (**1a**) was selected as a model substrate to optimize the reaction conditions. The reactions were carried out under different conditions by changing the molar ratio of substrate to $NaBrO_3$ and also the v/v amount of [bmim]HSO_4 to water as an additive. The reactions were carried out both at room temperature and at higher temperatures. The products expected from oxidation of hydrobenzoin are benzoin and benzil. The aim was to identify reaction conditions so that selective oxidation of hydrobenzoin to benzoin or benzyl could be achieved. The details of reactions carried out for optimization are listed in Table 1, entries 1–10. The reactions were attempted using 1.0 mmol of hydrobenzoin. It can be inferred from the listed reactions that water plays an important role in the selective oxidation of 1,2-diols to α-hydroxyketones or 1,2-diketones with sodium bromate in bmim[HSO_4].

Therefore, it is clear from above results of Table 1 that the selective oxidation of hydrobenzoin to benzoin could be achieved using 1:3 molar ratio of substrate:$NaBrO_3$ and bmim[HSO_4]:H_2O (1:1, v/v) at room temperature and selective oxidation to benzil could be achieved by carrying out the reaction using 1:3 molar ratio of substrate:$NaBrO_3$ and bmim[HSO_4]:H_2O (3:1, v/v) at 60 °C. These optimized reaction conditions were then extended to a variety of aryl and alkyl 1,2-diols. These could be oxidized to the corresponding α-hydroxyketones (Scheme 1; Table 2) or 1,2-diketones (Scheme 2; Table 3) in high yields by changing the reaction conditions.

Scheme 1



Subsequently, oxidation of α-hydroxyketones was also attempted using 1:3 molar ratio of substrate:$NaBrO_3$ and bmim[HSO_4]:H_2O 3:1 (v/v) at 60 °C. All the α-hydroxyketones underwent oxidation under these conditions to give the corresponding 1,2-diketones in high yields (Scheme 3; Table 4).

The recyclability of the ionic liquid was also investigated. The recovered ionic liquid gave comparable yields of the product **3a** in second and third cycles. However, the yields decreased gradually in fourth and fifth cycles as shown in Fig. 1.

The scope of the reagent, $NaBrO_3$ in bmim[HSO_4], was also investigated for oxidation of alcohols. We observed that primary alcohols could be selectively oxidized to the corresponding aldehydes and secondary alcohols, both aromatic and aliphatic, underwent oxidation to the corresponding carbonyl compounds **5a–5p** (Table 5) in high yields using 1:3 molar ratio of substrate to $NaBrO_3$ and bmim[HSO_4]:H_2O 3:1 (v/v) at 60 °C (Scheme 4).

Table 1 Optimization of reaction conditions for the oxidation of hydrobenzoin with $NaBrO_3$/bmim[HSO_4]

Run	**1a**:$NaBrO_3$	[bmim]HSO_4:H_2O[a] (v/v)	Temp./°C	Time	Product (yield/%)[b]
1	1:1	4:0	r.t.	6 h	–[c]
2	1:3	0:4	r.t.	6 h	No reaction
3	1:2	4:0	r.t.	6 h	–[c]
4	1:2	1:1	r.t.	6 h	**2a** + **3a**[d]
5	1:3	1:1	r.t.	30 min	**2a** (88)
6	1:3	1:3	r.t.	6 h	**2a** + **3a**[d]
7	1:3	3:1	r.t.	30 min	**2a** + **3a**[e]
8	1:3	1:1	60	4 h	**2a** + **3a**[e]
9	1:3	3:1	60	30 min	**3a** (87)
10	1:4	3:1	60	35 min	**3a** (86)
11	1:3	3:1	100	30 min	**3a** (85)

[a] For 1.0 mmol of substrate, 4 cm^3 of solvent was used

[b] **2a** = Benzoin; **3a** = Benzil

[c] Incomplete reaction; number of products

[d] Incomplete reaction

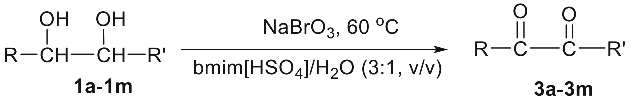
[e] Reaction complete

Table 2 Selective oxidation of 1,2-diols to α-hydroxyketones with $NaBrO_3$ (1:3 molar ratio) in bmim[HSO_4]:H_2O (1:1,v/v) at room temperature

Entry	Substrate	Product	Time/min	Yield/%	M.p./°C (obs.)	M.p./°C (lit.)
1	**1a**	**2a**	30	88	128–130	133–135 [25]
2	**1b**	**2b**	75	76	86–88	86–88 [25]
3	**1c**	**2c**	90	80	110–112	112–113 [26]
4	**1d**	**2d**	60	72	80–82	88–90 [26]
5	**1e**	**2e**	50	74	74–76	75–76 [27]
6	**1f**	**2f**	60	70	90–92	94–96 [27]
7	**1g**	**2g**	90	78	72–74	76–77 [26]
8	**1h**	**2h**	90	78	62–64	63–64 [28]

For 1 mmol of substrate, 4 cm^3 of solvent was used

Scheme 2



1a-1m **3a-3m**

a, R = R' = C_6H_5
b, R = R' = 4-ClC_6H_4
c, R = R' = 4-$MeOC_6H_4$
d, R = R' = 4-MeC_6H_4
e, R = R' = 3-ClC_6H_4
f, R = R' = 4-BrC_6H_4
g, R = R' = 2-MeC_6H_4
h, R = R' = 2-ClC_6H_4
i, R = R' = 2-BrC_6H_4
j, R = R' = 2-$MeOCC_6H_4$
k, R = R' = 4-FC_6H_4
l, R = R' = -$(CH_2)_4$-
m, R = *n*-C_8H_{17}, R' = *n*-$C_7H_{14}COOH$

No over-oxidation of aldehydes to carboxylic acid was observed. However, aldehydes could be oxidised subsequently to the corresponding carboxylic acids on addition of 1:3 molar ratio of substrate to $NaBrO_3$ and bmim[HSO_4]:H_2O 3:1 (v/v).

Conclusion

In conclusion, we have developed a simple and convenient procedure for the selective oxidation of 1,2-diols, α-hydroxyketones, and alcohols using BrO_3^- anion as an oxidant and bmim[HSO_4] as a solvent and co-catalyst. We have also shown the selectivity and efficiency of bromate anion as an oxidant. Moreover, ionic liquid used could be recycled three times without any significant loss of activity. Easy work-up, mild conditions and high yields of products make this method a benign alternative to the present methodologies.

Experimental

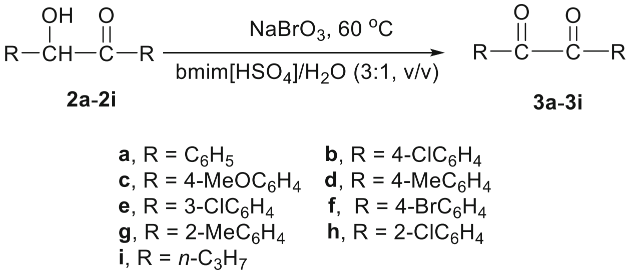
All the melting points were recorded on a Tropical Labequip apparatus. IR spectra were recorded on Perkin-Elmer FT-IR SPECTRUM-2000 and NMR spectra were recorded

Table 3 Oxidation of 1,2-diols to 1,2-diketones with $NaBrO_3$ in bmim[HSO_4]: H_2O (3:1,v/v) at 60 °C

Entry	Substrate	Product	Time/min	Yield/%	M.p./°C (obs.)	M.p./°C (lit.)
9	**1a**	**3a**	25	88	90–92	92–94 [8]
10	**1b**	**3b**	25	87	198–200	198–199 [8]
11	**1c**	**3c**	45	84	130–132	132–133 [8]
12	**1d**	**3d**	30	89	104–106	104–105 [8]
13	**1e**	**3e**	60	82	116–118	116–117 [29]
14	**1f**	**3f**	40	81	224–226	226–228 [8]
15	**1g**	**3g**	45	78	90–92	91–93 [30]
16	**1h**	**3h**	60	80	132–134	134–135 [8]
17	**1i**	**3i**	45	82	128–130	128–130 [8]
18	**1j**	**3j**	40	80	126–128	129–130 [31]
19	**1k**	**3k**	50	78	116–118	118 [32]
20	**1l**	**3l**	30	72	Liquid	– [33]
21	**1m**	**3m**	40	78	84–86	82–83 [8]

For 1 mmol of substrate, 4 cm^3 of solvent was used

Scheme 3



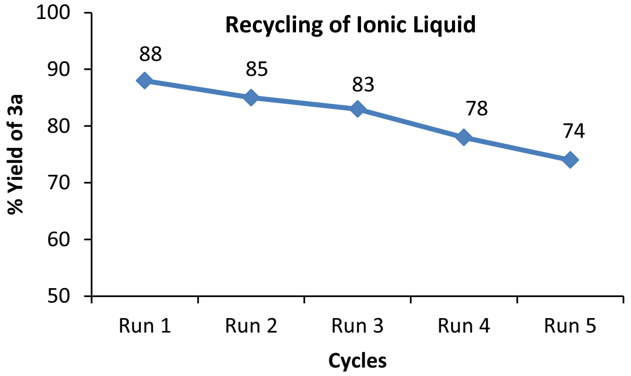


Fig. 1 Recycling yields: reaction of hydrobenzoin (1.0 mmol) with $NaBrO_3$ (3.0 mmol) in [bmim]HSO_4 (3:1, v/v) at 60 °C

on a Hitachi FT-NMR model R-600 (60 MHz) with TMS as internal standard. All the products are known and were identified by co-TLC with authentic samples whenever available, m.p., IR and NMR spectra.

General procedure for the oxidation of 1,2-diols to α-hydroxyketones

In a typical reaction, a mixture of hydrobenzoin (**1a**, 1.0 mmol) and sodium bromate (3.0 mmol) was placed in a 50 cm^3 RB flask fitted with a condenser and a magnetic stir bar. Ionic liquid and water, [bmim]HSO_4:H_2O (1:1, v/v) (4 cm^3) was added to the flask. The reaction mixture was stirred at room temperature. The progress of the reaction was monitored by TLC, using petroleum ether: ethyl acetate (80:20, v/v) as eluent. After completion of the reaction, the product was extracted with diethyl ether (3 × 15 cm^3). The combined ether extract was washed with saturated solution of $Na_2S_2O_3$ to decompose excess bromine and water (2 × 10 cm^3). The combined ether layer was dried over anhyd. Na_2SO_4 and concentrated on a rotary evaporator to give the product. The crude product was recrystallised from aqueous ethanol and yielded pure benzoin (**2**) as characterized by m.p., IR and ^{1}H NMR spectra.

The aqueous layer containing ionic liquid was washed with diethyl ether and reactivated at 80 °C under vacuum. The recovered ionic liquid could be reused for the reactions for up to three runs without any appreciable loss of efficiency.

General procedure for the oxidation of 1,2-diols, α-hydroxyketones and alcohols to 1,2-diketones and aldehydes/ketones

In a typical experiment, a mixture of 1,2-diols/α-hydroxyketones/alcohols (1 mmol), sodium bromate (3 mmol), and bmim[HSO_4]:H_2O 3:1 (v/v) along with a stir bar was placed in a RB flask fitted with a condenser. The reaction mixture was stirred magnetically in an oil-bath maintained at 60 °C for an appropriate time as mentioned in Tables 3, 4, and 5, respectively. After completion of the reaction, as

Table 4 Oxidation of α–hydroxyketones to 1,2-diketones with $NaBrO_3$ (1:3 molar ratio) in bmim[HSO_4]:H_2O (3:1,v/v) at 60 °C

Entry	Substrate	Product	Time/min	Yield/%	M.p./°C (obs.)	M.p./°C (lit.)
1	**2a**	**3a**	25	86	90–92	92–94 [8]
2	**2b**	**3b**	25	80	196–198	198–199 [8]
3	**2c**	**3c**	30	82	132–134	132–133 [8]
4	**2d**	**3d**	35	84	104–106	104–105 [8]
5	**2e**	**3e**	40	83	116–118	116–117 [34]
6	**2f**	**3f**	45	81	224–226	226–228 [8]
7	**2g**	**3g**	40	85	90–92	91–93 [30]
8	**2h**	**3h**	47	78	132–134	134–135 [8]
9	**2i**	**3n**	60	74	Liquid	– [35]

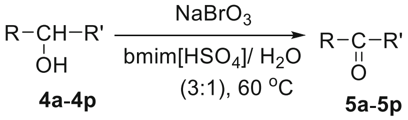
For 1 mmol of substrate, 4 cm^3 of solvent was used

Table 5 Oxidation of alcohols with $NaBrO_3$ in bmim[HSO_4]:H_2O (3:1,v/v) at 60 °C

Entry	Substrate	Product	Time/min	Yield/ %	M.p./ °C (obs.)	M.p./ °C (lit.)
1	4a	**5a**	45	87	82–84	82–83 [36]
2	4b	**5b**	35	82	46–48	47–49 [37]
3	4c	**5c**	60	84	76–78	79–80 [38]
4	4d	**5d**	45	82	142–144	144–145 [39]
5	4e	**5e**	40	82	42–44	48–52 [37]
6	4f	**5f**	90	80	Liquid	– [40]
7	4g	**5g**	45	74	Liquid	– [41]
8	4h	**5h**	45	70	Liquid	– [42]
9	4i	**5i**	40	72	Liquid	– [43]
10	4j	**5j**	60	69	100–102	100–105 [44]
11	4k	**5k**	30	65	Liquid	– [45]
12	4l	**5l**	30	78	Liquid	– [46]
13	4m	**5m**	35	76	Liquid	– [46]
14	4n	**5n**	30	81	Liquid	– [46]
15	4o	**5o**	30	74	Liquid	– [47]
16	4p	**5p**	45	78	Liquid	– [48]

For 1 mmol of substrate 4 cm^3 of solvent was used

Scheme 4



a, R = R' = 9-Fluorenyl
b, R = R' = C_6H_5
c, R = C_6H_5, R' = 4-BrC_6H_4
d, R = R' = 4-ClC_6H_4
e, R = 4-BrC_6H_4, R' = Me
f, R = 4-ClC_6H_4, R' = Me
g, R = R' = C_2H_5
h, R = C_6H_{13} R' = CH_3
i, R = R' = *n*-C_3H_7
j, R = 9-Anthryl, R' = H
k, R = 1-Naphthyl, R' = H
l, R = 4-ClC_6H_4, R' = H
m, R = 4-$MeOC_6H_4$, R' = H
n, R = 4-BrC_6H_4, R' = H
o, R = *n*-C_7H_{15}, R' = H
p, R = *n*-C_8H_{17}, R' = H

monitored by TLC using petroleum ether:ethyl acetate (80:20, v/v) as eluent, the reaction mixture was cooled to room temperature and worked up as mentioned above. The product obtained was identified by m.p (wherever applicable), IR and NMR spectra.

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