

Ionic liquid promoted selective oxidation of organic compounds with NaBrO_3

Ahmad Shaabani, Elham Farhangi, Abbas Rahmati

Department of Chemistry, *Shahid Beheshti* University, Tehran, Iran

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Abstract 1-Butyl-3-methylimidazolium bromide ($[\text{bmim}]\text{Br}$) as an ionic liquid promoted selectively the oxidation of alkyl arenes and alcohols to the corresponding carbonyl compounds with NaBrO_3 in excellent yields under neutral conditions at the 70°C . Among the various ionic liquids examined, the $[\text{bmim}]\text{Br}$ exhibited the best performances with NaBrO_3 . The ionic liquid can be recycled and reused for several runs without any significant loss of activity.

Keywords 1-Butyl-3-methylimidazolium bromide; Oxidation; Alkylarene; Alcohol.

Introduction

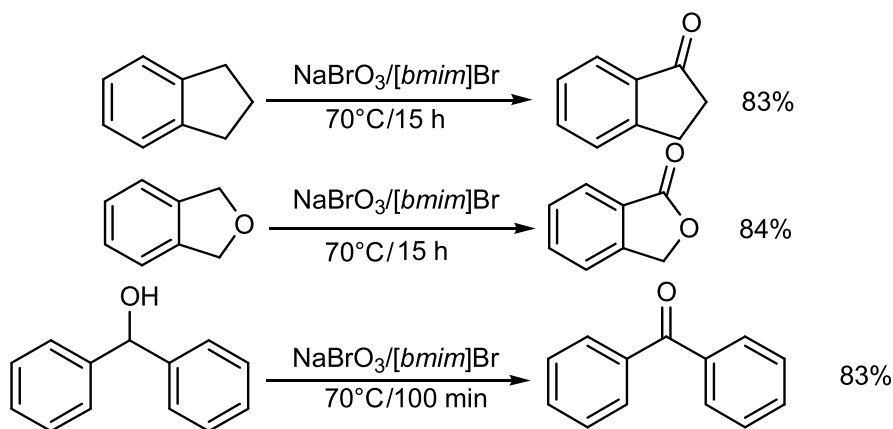
Oxidation reactions are among the most important transformations in synthesis chemistry and offer an important methodology for the introduction and modification of functional groups. During the last two decades, there has been a spectacular development in the field and a large number of novel and useful oxidation reactions have been discovered. The oxidation of alkyl arenes and alcohols to their corresponding carbonyl compounds is of significant importance in organic chemistry, both for fundamental research and industrial manufacturing. The world-wide annual production of carbonyl compounds is over 1×10^7 tons and most of these compounds are produced from the oxidation of alkyl arenes and alcohols [1–8].

Sodium bromate is commercially available as an inexpensive stable solid, which potentially is an interesting candidate for the oxidation of organic compounds because of its capability in multi-electron transfer. Although sodium bromate is thermodynamically a strong oxidant, according to literature bromate itself is not able to oxidize organic compounds.

The standard redox potential of the bromate ion, BrO_3^- , is 0.61 V in neutral and alkaline aqueous solution while in aqueous acidic media it has a potential of 1.52 V. Due to the low standard redox potential in neutral or weak acidic media and very low solubility in most of organic solvents, it is usually used in aqueous media in the presence of strong acidic co-reactants, such as NaHSO_3 [9–12], HBr [13], cerium(IV) ammonium nitrate (CAN) [14, 15], H_2SO_4 [16, 17], KHSO_4 [18], Bu_4NHSO_4 [19], HClO_4 [20], $\text{Mg}(\text{HSO}_4)_2$ [21], silica sulfuric acid [22], and cation exchange resin [23].

In spite of their potential utility and solubility in these media, most of these homogeneous acids present limitations due to use of corrosive reagents, tedious work-up procedures, the necessity of neutralization of strong acidic media, and producing undesired washes. In addition, the high acidity of solution not only increased the oxidizing power of BrO_3^- and restricted to apply this reagent for the selective oxidation of most of organic compounds, but due to bromine generation under acidic conditions in the presence of reducing agents [24–27], the main products becomes contaminated by the formation of α -bromo substituted of the corresponding carbonyl

Correspondence: Ahmad Shaabani, Department of Chemistry, *Shahid Beheshti* University, P.O. Box 19839-4716, Tehran, Iran. E-mail: a-shaabani@cc.sbu.ac.ir



Scheme 1

compounds. So, due to bromine generation, the reaction mixture must be neutralized with sodium thio-sulfate before isolating the product. Furthermore, in most of these oxidation systems the removal of excess sodium bromate from the reaction mixture and separation of bromate or bromide from co-reactant salts is difficult.

Therefore, the development of new approaches for the selective oxidation of organic compounds with NaBrO_3 in the absence of acidic co-reactants in non-aqueous media is of some importance in synthesis organic compounds.

One can wonder whether inert ionic liquids are useful solvents for NaBrO_3 -mediated organic transformations taking into account the popularity of ionic liquids as alternative solvents for organic reactions [28–35]. To the best of our knowledge, ionic liquids have not yet been explored for reactions with NaBrO_3 .

In continuation of our studies on the oxidation of organic compounds [24–26, 36–40], in this paper we evaluate various ionic liquids for BrO_3^- -mediated oxidation of alkyl arenes and alcohols under neutral conditions in non-aqueous media at 70°C (Scheme 1).

Results and discussion

In order to obtain the best ionic liquid, we examined various ionic liquids, such as 1-butyl-3-methylimidazolium bromide ($[\text{bmim}]\text{Br}$), 1-butyl-3-methylimidazolium chloride ($[\text{bmim}]\text{Cl}$), and 1-butyl-3-methylimidazolium hexafluorophosphat ($[\text{bmim}]\text{PF}_6$). Oxidation of fluorene to 9-fluorenone and benzoin to benzil were selected as model reactions. Test reactions were carried out by mixing of NaBrO_3 (0.50 g, 3.30 mmol) with various ionic

Table 1 Oxidation of fluorene and benzoin with NaBrO_3 in various ionic liquids at 70°C^a

Entry	Ionic liquid	Yield ^b /%	Yield ^b /%
1	$[\text{bmim}]\text{Br}$	92	90
2	$[\text{bmim}]\text{Cl}$	50	70
3	$[\text{bmim}]\text{PF}_6$	30	20

^a NaBrO_3 (0.5 g, 3.30 mmol); ionic liquid (0.30 g); fluorene or benzoin (1 mmol)

^b The yields of oxidation fluorene and benzoin after 8 h and 100 min

Table 2 Oxidation of fluorene and benzoin with NaBrO_3 in $[\text{bmim}]\text{Br}$ at various temperatures^a

Entry	Temperature/ $^\circ\text{C}$	Yield ^b /%	Yield ^b /%
1	25	0	0
2	50	50	40
3	70	92	90
4	90	95	90

^a NaBrO_3 (0.5 g, 3.30 mmol); $[\text{bmim}]\text{Br}$ (0.30 g, 1.37 mmol); fluorene or benzoin (1 mmol)

^b The yields of oxidizing fluorene and benzoin after 8 h and 100 min, respectively

liquids (0.30 g) followed by addition of fluorene (0.17 g, 1 mmol) or benzoin (0.21 g, 1 mmol). As indicated in Tables 1 and 2, 1-butyl-3-methylimidazolium bromide is the best suited ionic liquid for these reactions at 70°C in terms of yields and easy work-up.

As can be seen from Table 3, alkyl arenes are converted into the corresponding carbonyl compounds in good yields under very mild reaction conditions. The products are identical to those obtained under heterogeneous conditions where the reductant is dis-

Table 3 Oxidation of alkyl arenes to carbonyl compounds with NaBrO₃/[bmim]Br at 70°C

Entry	Reductant	Product	Time/h	Yield ^a /%	Mp or Bp (reported) ^b /°C
1	ethylbenzene	acetophenone	10	75	18–19 (19–20) ^b
2	propylbenzene	propiophenone	11	79	17–18 (17–19) ^b
3	butylbenzene	1-phenyl-1-butanone	13	78	11–12 (11–13) ^b
4	diphenylmethane	benzophenone	17	79	48–49 (47–49) ^b
5	fluorene	9-fluorenone	8	92	80–81 (80–83) ^b
6	indane	1-indanone	15	83	39–40 (39–41) ^b
7	tetralin	α -tetralone	10	85	6–7 (2–7) ^b
8	1,3-dihydro isobenzofuran	phthalide	15	84	71–72 (70–73) ^c
9	xanthene	9-xanthenone	9	90	173–174 (172–174) ^b
10	<i>p</i> -xylene	4-methylbenzoic acid	12	72	178–179 (177–180) ^b

^a Isolated yields^b Ref. [41]^c Ref. [42]**Table 4** Oxidation of alcohols to carbonyl compounds with NaBrO₃/[bmim]Br at 70°C

Entry	Reductant	Product	Time/h	Yield ^a /%	Mp or Bp (reported) ^b /°C
1	cyclohexanol	cyclohexanone	180	79	153–155 (154–156) ^b
2	cyclooctanol	cyclooctanone	150	91	75–77 (77–79) ^b
3	cyclodecanol	cyclodecanone	150	88	23–24 (21–24) ^b
4	4-methylbenzyl alcohol	4-methyl benzaldehyde	100	81	202–203 (204) ^d
5	4-methoxybenzyl alcohol	4-methoxy benzaldehyde	100	79	247–248 (247–249) ^d
6	4-chlorobenzyl alcohol	4-chloro benzaldehyde	90	83	47–48 (45–50) ^b
7	4-nitrobenzyl alcohol	4-nitro benzaldehyde	90	85	105–106 (104–106) ^b
8	1-phenylethanol	acetophenone	180	76	18–19 (19–20) ^b
9	1-indanol	1-indenone	140	87	39–40 (39–41) ^b
10	diphenylmethanol	benzophenone	100	83	48–49 (47–49) ^b
11	benzoin	benzil	100	90, 91, 87 ^c	94–95 (94–96) ^b
12	4,4'-dimethoxy benzoin	4,4'-dimethoxy benzil	80	92	132–133 (132–134) ^b
13	9-fluorenyl methanol	9-fluorenone	140	86	80–81 (80–83) ^b

^a Isolated yields^b Ref. [41]^c The same IL was used for each of the three runs^d Ref. [42]

solved in an inert solvent; however, the reaction times are reduced from a few days to a few hours at 70°C. As indicated in Scheme 1, the reaction is equally effective when oxygen is present in the side chain. Excellent yields of the corresponding lactones are realized when the side chain is an exocyclic ether. Some alkyl arenes, such as indane and tetralin are readily oxidized to their corresponding carbonyl compounds (entries 1–9), whereas others such as xylene are converted to their corresponding carboxylic acids (entry 10).

As indicated in Scheme 1, secondary alcohols are converted into the corresponding ketones in good yields (Table 4), and aldehydes are obtained in comparable yields from the oxidation of primary alcohols (entries 4–7, Table 4). The preparation of aromatic

aldehydes from the corresponding primary alcohols has not previously been easily achieved using permanganate or other strong oxidants because aldehydes are so readily converted to carboxylic acids under oxidizing conditions. Among the various alcohols studied, α -hydroxyketones were found to be the most reactive and needed shorter reaction times for their oxidation (Table 4, entries 11 and 12).

One of the advantages of ionic liquids is their ability to function as a recyclable reaction medium. We were able to separate [bmim]Br from the reaction medium easily by extracting the product with *n*-hexane and washing the residue with dichloromethane, evaporating it under vacuum, and reuse it for subsequent reactions (entry 11, Table 4).

In conclusion, we developed an efficient and simple procedure for selective oxidation of organic compounds using BrO_3^- as oxidant and $[\text{bmim}]\text{Br}$ as an ionic liquid. Most importantly, the $[\text{bmim}]\text{Br}$ could also be recycled and reused in further reactions without any significant loss of activity. This method possesses increased compatibility with different functional groups and the oxidation reaction is carried out in neutral conditions. Unlike previously reported methods, this one requires neither acids as co-oxidant nor protic solvents, such as water. Further applications of this reagent combination are under investigation in our laboratory.

Experimental

Melting points were measured on an Electrothermal 9200 apparatus. IR spectra were recorded on FT-IR 102MB BOMEM apparatus. Mass spectra were recorded on a FINNIGAN-MAT 8430 mass spectrometer operating at an ionization potential of 70 eV. ^1H NMR spectra were recorded on a BRUKER DRX-300 AVANCE spectrometer at 300.13 MHz. ^1H NMR spectra were obtained on solutions in CDCl_3 .

All of the products of these reactions are known compounds and were characterized from their IR and ^1H NMR spectra and by comparison of their melting points (or those of the derivatives) with known compounds [40]. Most importantly, no over-oxidized product was detected by ^1H NMR analysis of the crude reaction mixture in all the cases.

Oxidation of alkyl arenes or alcohols: general procedure

In a typical reaction, a mixture of 1 mmol alkyl arene or alcohol and 0.50 g sodium bromate (3.30 mmol) was successively added to a screw-capped vial containing a magnetic stirring bar to 0.30 g $[\text{bmim}]\text{Br}$ (1.37 mmol) and was heated at 70°C in a preheated oil bath, while the progress of the reaction was followed by TLC and GC. Upon completion, the reaction mixture was washed with *n*-hexane. Evaporation of the solvent gave a product of sufficient purity for most purposes.

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