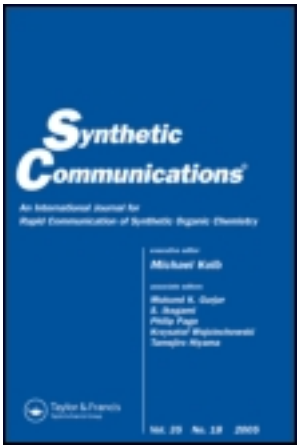

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Efficient Procedure for Oxidation of Benzylic Alcohols to Carbonyl Compounds by N-Bromosuccinimide in Ionic Liquid

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Efficient Procedure for Oxidation of Benzylic Alcohols to Carbonyl Compounds by *N*-Bromosuccinimide in Ionic Liquid

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Abstract: Efficient oxidation of various benzylic alcohols to the corresponding carbonyl compounds has been achieved in the presence of NBS and 2,6-lutidine in ionic liquid [bmim]BF_4.

Keywords: Benzylic alcohols, carbonyl, ionic liquid, oxidation

The oxidation of benzylic alcohols to carbonyl compounds is an important reaction in organic synthesis and numerous methods have been developed for this conversion. For example, recent reports on this transformation have dealt with the utilization of nitric acid,[1] DMSO/HBr,[2] [hydroxy(tosyloxy) iodo]benzene,[3] and iodobenzene diacetate on alumina.[4] A readily available and stable *N*-bromosuccinimide (NBS) also has been utilized in the oxidation of alcohols and results were well documented.[5] Representative methods include the efficient oxidation of alcohols with a NBS/tetrabutylammonium iodide system[6] and conversion of 1,2-diols to 1,2-diketones in the presence of NBS/pyridine.[7] However, these NBS-mediated oxidation methods always utilized environmentally undesirable organic solvents such as acetonitrile or carbon tetrachloride.

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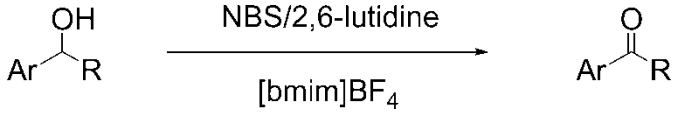
In the past decade, ionic liquids have been received substantial attention in organic synthesis because of their environmentally benign nature, high polarity, and good thermal stability.[8,9] Often shorter reaction times, high yields, cleaner reaction products, and high selectivities are obtained from ionic-liquid reaction media. A couple of methods have been reported for the oxidation of alcohols conducted in ionic liquids.[10,11] As a part of our program related to development of environmentally benign synthetic methodology, we now report oxidation of benzylic alcohols promoted by NBS in an ionic liquid. As far as we are aware, the NBS-mediated oxidation of alcohols in an ionic liquid medium has not been reported to date. Treatment of benzylic alcohols with *N*-bromosuccinimide (1.2 equiv) and 2,6-lutidine (1.0 equiv) in 1 mL of 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim]BF_4) ionic liquid at 40°C for 0.5–3 h readily afforded the corresponding carbonyl derivatives (Scheme 1). When the ionic liquid medium was changed from (bmim)BF_4 to more hydrophobic (bmim)PF_6, the reactions gave less satisfactory results with much lower yields. It also turned out the use of a base was necessary in the reaction conditions. In the absence of a base, the reactions provided the desired carbonyl compounds along with significant amount of benzylic bromide side products. We explored the effect of the base on the oxidation reactions utilizing various bases such as triethylamine; pyridine; 2,6-lutidine; DBU; and potassium carbonate and found that among these bases, 2,6-lutidine afforded the best result in terms of cleanness and reaction times. The oxidation of both primary and secondary benzylic alcohols occurred equally well to provide the corresponding carbonyl compounds in high to excellent yields in short reaction times. The results are summarized in Table 1.

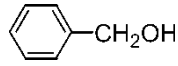
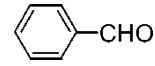
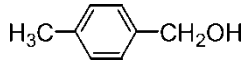
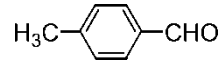
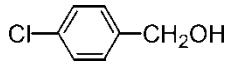
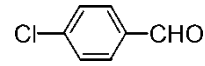
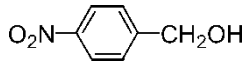
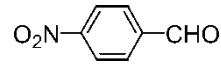
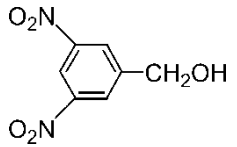
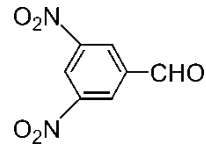
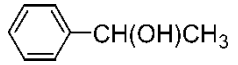
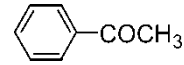
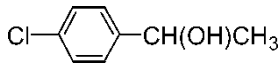
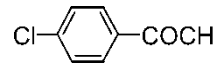
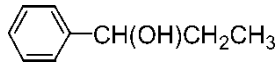
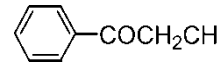
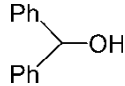
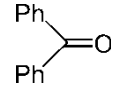
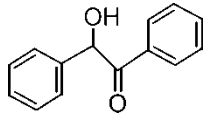
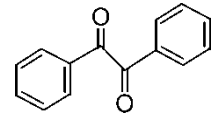
The competitive aromatic bromination has not been observed in all of the cases tested. The benzhydrol and benzoin are smoothly oxidized to the corresponding carbonyl compounds in high yields under present reaction conditions (entries **9** and **10**). It is also noteworthy that prolonged reaction times were required in cases of benzylic alcohols with electron-withdrawing groups on the aromatic rings. This result can be rationalized by the sluggish formation of hypoboromite reaction intermediates in cases of the less reactive electron-deficient benzylic alcohols.

In summary, we have discovered a novel and efficient method for the oxidation of benzyl alcohols into the corresponding carbonyl compounds utilizing an NBS/2,6-lutidine system in (bmim)BF_4 ionic liquid.



Scheme 1.

Table 1. Oxidation of benzylic alcohols with NBS in [bmim]BF_4

Entry	Substrate	Product	Time (h)	Yield (%)[a]
1			0.5	98
2			0.5	95
3			1	91
4			2	93
5			4	85
6			1	98
7			2	92
8			1	93
9			2.5	88
10			3	87

[a]Isolated yield.

EXPERIMENTAL

The 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim]BF_4) was obtained from Fluka. IR spectra were recorded on a Jasco FT/IR 5300 spectrophotometer using KBr optics. ^{1}H NMR spectra were recorded on a Varian 2000 (300-MHz) spectrometer in $CDCl_3$ using TMS as internal standard. Merck silica gel 60 (230–400 mesh) was used for flash column chromatography.

General procedure for benzylic oxidation reaction using NBS: To a stirred solution of benzylic alcohol (1.0 mmol) in (bmim)BF_4 (1 mL) was added *N*-bromosuccinimide (0.214 g, 1.2 mmol) and 2,6-lutidine (0.107 g,

1.0 mmol), and stirring was continued at 40°C for the time indicated in the Table 1. After completion of the reaction, the product was extracted with dichloromethane (2 × 25 mL), washed with water (40 mL), and dried over $MgSO_4$. The solvent was removed in vacuo and the crude mixture was purified by silica-gel chromatography using ethyl acetate–hexane (1:2) to give the pure carbonyl compound.

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