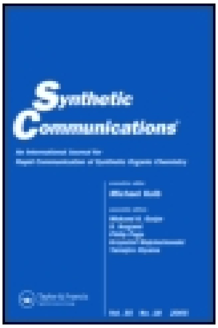

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Phosphonium Ionic Liquid: A Novel Catalyst for Benzyl Halide Oxidation

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Phosphonium Ionic Liquid: A Novel Catalyst for Benzyl Halide Oxidation

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Sandesh S. Modani, Jayant J. Bhale, Sumangala B. Tathe,
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Abstract: An environmentally friendly ionic liquid is used for the first time in mild and selective oxidation of aryl halides to corresponding aldehydes using iodoxybenzoic acid as oxidizing agent.

Keywords: Aryl halides, carbonyl compounds, hypervalent iodine, ionic liquids, selective oxidation

INTRODUCTION

Oxidation of aryl halide to aldehyde is an important transformation in synthetic organic chemistry. Different reagents have been used for this transformation.[1,2] However, all these procedures are associated with certain limitations like long reaction times, poor yields, high temperatures, and so on. Thus the introduction of a new method for the oxidation of aryl halides is still in demand.

In past two decades, applications of hypervalent iodine have been proliferating in synthetic organic chemistry.[3] Among various hypervalent iodine reagents, *o*-iodoxy benzoic acid (IBX) is used as a versatile oxidizing agent[4] because of its mild, selective, efficient, and ecofriendly

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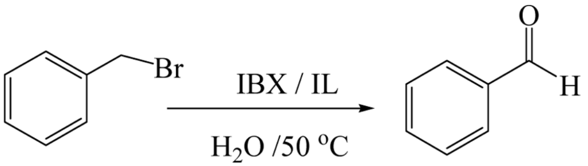


Scheme 1.

properties and operational simplicity. Recently, SIBX (stabilized formulation of IBX) has been used for the efficient and selective oxidation of alcohol in presence of aq. sodium bicarbonate solution.[5] Oxygen-mediated oxidation of alkenes using nafion-supported platinum(II) terpyridyl acetylide complex using a photosensitization reaction has also been reported.[6]

Nonvolatile ionic liquids have been recognized as environmentally benign alternatives to volatile organic solvents.[7] They possess high thermal stability and good solvating ability. Their immiscibility with organic solvents permits development of a heterogeneous system to carry out the reaction. The products formed are recovered by a liquid–liquid extraction process.[8] Recently, the oxidation of alcohols and diols has been reported using imidazoliun ionic liquids.[9,10]

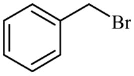
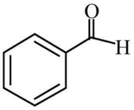
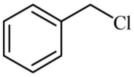
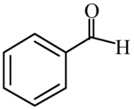
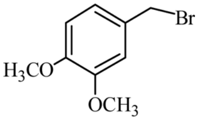
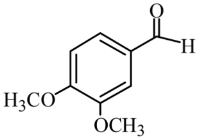
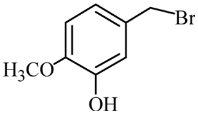
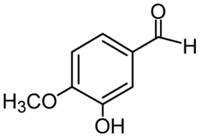
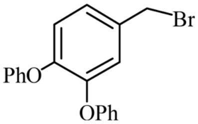
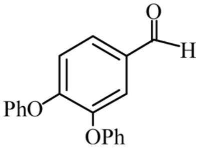
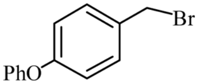
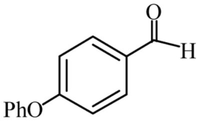
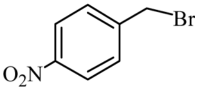
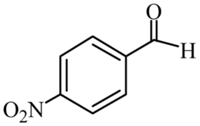
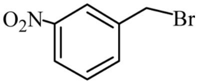
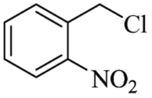
In the present work, for first time we introduce a new methodology for the oxidation of aryl halide to corresponding carbonyl compounds using IBX oxidant in the presence of phosphonium salt ionic liquid and water (Scheme 1). The reaction completes in a short time, affording the product in excellent yield.

RESULTS AND DISCUSSION

In a typical condensation reaction, a mixture of aryl halide **1** (1 equiv.), IBX **2** (1.5 equiv.), phophonium ionic liquid (1 ml), and water (2 ml) was heated at 50°C for the appropriate time (Table 1). After completion of the reaction as indicated by thin-layer chromatography (TLC), by usual workup the corresponding pure carbonyl compound **3** was obtained in excellent yield. The aqueous layer was dried at 120°C, and the residual ionic liquid was recycled and reused several times. When carried out in water without phosphonium ionic liquid, the same reactions do not proceed even after 5 h of heating at 50°C (Table 2).

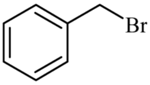
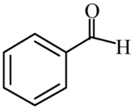
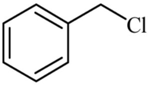
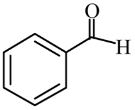
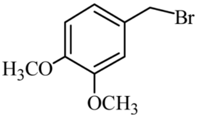
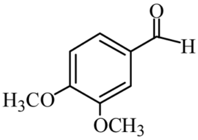
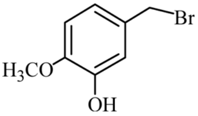
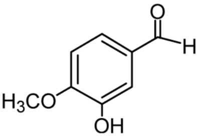
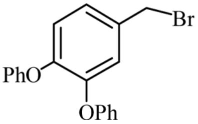
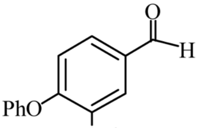
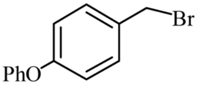
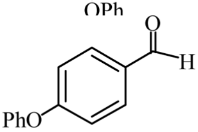
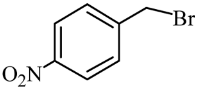
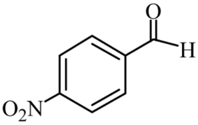
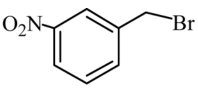
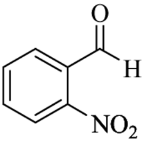
The oxidation of aryl halides has been done using IBX as oxidizing agent. The reaction, carried out in water medium, avoids the hazardous organic solvents, which not only reduces the cost of the product but is

Table 1. Conversion of aryl halides to carbonyl compounds in ionic liquid

Substrate	IBX (eq.)	Temp (°C)	Yield (%)	Time (Min)	Product
	1.5	50	92	20	
	1.5	50	88	20	
	1.5	50	89	30	
	1.5	50	92	55	
	1.5	50	91	40	
	1.5	50	92	40	
	1.5	50	91	45	
	1.5	50	89	35	

also helpful for environmental safety. In this transformation, we used trihexyl (tetradecyl) phosphonium tetrafluroborate as a phosphonium ionic liquid. The advantage of phosphonium ionic liquid is its easy availability and relatively low cost. This ionic liquid is thermally and chemically stable. It is recycled and reused about 10 to 20 times with slight change in its efficiency (0.5–1%). Trihexyl (tetradecyl)

Table 2. Conversion of aryl halides to carbonyl compounds without ionic liquid in water

Substrate	IBX (eq.)	Temp (°C)	Yield (%)	Time (min.)	Product
	1.5	50	—	300	
	1.5	50	Trace amount	300	
	1.5	50	—	300	
	1.5	50	—	300	
	1.5	50	—	300	
	1.5	50	—	300	
	1.5	50	—	300	
	1.5	50	—	300	

phosphonium tetrafluroborate ionic liquid is less dense than water. Thus, just decanting aqueous streams can easily separate the product. In addition, the imidazolium ionic liquids are slightly acidic, which may result in carbene formation. However, the phosphonium ionic liquid does not possess any acidic protons, so no carbene formation takes place. Hence, 100% utility of this ionic liquid can be achieved by using it in organic transformations.

The oxidation of nonsubstituted aryl halide to the carbonyl compound completes in a short time. However, the conversion of substituted aryl halide into the carbonyl compound requires somewhat longer time. The product formation in this transformation is excellent (85–92%, Table 1).

The reaction of electron-rich aryl halide proceeds via unimolecular nucleophilic substitution (SN^1) mechanism and leads to the addition product by salt formation. However, the electron-deficient aryl halide reaction proceeds via a bimolecular nucleophilic substitution reaction (SN^2) mechanism. Further, the addition product decomposes to carbonyl compound, forming iodoso benzoic acid (IBA) as a by-product.

In accordance with the mechanism, only 1 equivalent of IBX is sufficient for the oxidation of benzyl bromide. Excess IBX addition does not afford great yield of the product. Benzyl chloride reacted only sluggishly, leading to poor isolated yield. Observation of the reaction shows initially generated HX is quite detrimental to IBX. The IBX in reaction reduces to *o*-iodoso benzoic acid in saturated hydrogen halide (HX). A further complication is that the *o*-iodoso benzoic acid, the product of partial IBX reduction, may compete with benzyl halide to afford undesirable ethers. The conversion is extremely good when the halide iodine is taken. It increases the reaction rate, which obviates the reduction of IBX in situ–generated HX.

EXPERIMENTAL PROCEDURE OF BENZALDEHYDE SYNTHESIS

A mixture of benzyl bromide (0.171 g; 1 mmol), iodoxybenzoic acid (0.420 g; 1.5 mmol), trihexyl (tetradecyl) phosphonium tetrafluroborate (1 ml) and water (2 ml) were stirred at 50°C under a nitrogen atmosphere for the appropriate time. After completion of reaction as determined by TLC, the reaction mixture was diluted with water and then extracted with ethyl acetate solvent (3 × 10 ml). The solvent ethyl acetate was evaporated, and the crude was purified by silica-gel chromatography using petroleum ether–ethyl acetate (3:2) mixture as an eluent. Similarly, the other aldehydes were also prepared using the same method (Table 1).

The aqueous layer was further heated at 120°C to remove the water, and the residual ionic liquid was recycled and reused several times without any change in their efficiency (Table 3).

Table 3. Recovery of ionic liquid in carbonyl compound synthesis

				Yield (%) of recovered ionic liquid		
Entry	Aryl halide	Product	Time (min)	Cycle 1	Recycle 1	Recycle 2
1	1a	3a	20	93	93	92
2	1b	3b	20	90	89	89

SPECTRAL DATA

^{1}H NMR and ^{13}C NMR spectra were recorded at room temperature on a Varian Inova spectrometer in $CDCl_3$ using tetramethylsilane (TMS) as internal standard.

2-Nitro Benzaldehyde

^{1}H NMR ($CDCl_3$): δ 7.7 (dd, 1 H, Ar-H), 7.8 (dd, 1 H, Ar-H), 7.9 (dd, 1 H, Ar-H), 8.1 (dd, 1 H, Ar-H), 10.4 (s, 1 H, CHO). ^{13}CNMR ($CDCl_3$): 124.2 (2C, Ar), 130.4 (2C, Ar), 139.9 (1C, Ar), 150.9 (1C, Ar), 190.3 (1C, CHO).

3-Hydroxy-4-methoxy Benzaldehyde

^{1}H NMR ($CDCl_3$): δ 3.9 (s, 3 H, OCH_3), 6.0 (s, 1 H, OH), 6.9 (dd, 1 H, Ar-H), 7.2 (s, 1 H, Ar-H), 7.4 (dd, 1 H, Ar-H), 9.85 (s, 1 H, CHO). ^{13}CNMR ($CDCl_3$): 56.1 (1C, OCH_3), 110.1 (1C, Ar), 113.9 (1C, Ar), 124.6 (1C, Ar), 130.4 (1C, Ar), 146.1 (1C, Ar), 151.8 (1C, Ar), 191.1 (1C, CHO).

CONCLUSIONS

In summary, we have demonstrated an efficient and mild protocol for the selective oxidation of aryl halides to corresponding aldehyde using IBX as oxidizing agent in the presence of phosphonium ionic liquid. The method offers several advantages such as good yields, shorter reaction time, cleaner reaction profiles, and simple experimental and workup procedures.

ACKNOWLEDGMENT

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REFERENCES

1. Chandrasekhar, S.; Sridhar, M. A. A. Bifunctional approach towards the mild oxidation of organic halides: 2-Dimethylamino-N,N-dimethylaniline N-oxide. *Tetrahedron Lett.* **2000**, *41*, 5423–5425.
2. Itoh, A.; Kodon, T.; Inagaki, S.; Masaki, Y. Photooxidation of arylmethyl bromides with mesoporous silica FSM-16. *Org. Lett.* **2000**, *2*, 2455–2457.
3. (a) Tohma, H.; Takizawa, S.; Maegawa, T.; Kita, Y. Facile and clean oxidation of alcohols in water using hypervalent iodine (III) reagents. *Angew. Chem. Int. Ed.* **2000**, *39*, 1306; (b) Togo, H.; Nabona, T.; Yanaguehi, K. Preparation and reactivities of novel (diacetoxyiodo)arenes bearing heteroaromatics. *J. Org. Chem.* **2000**, *65*, 8391.
4. (a) Wirth, T. IBX—New reactions with an old reagent (highlight). *Angew. Chem. Int. Ed.* **2001**, *40*, 2812–2814; (b) Nicolaou, K. C.; Baran, P. S.; Zhong, Y. L.; Barlueng, S.; Hunt, W. K.; Kranich, R.; Vega, J. A. Iodine(V) reagents in organic synthesis, part 3: New routes to heterocyclic compounds via *o*-iodoxybenzoic acid–mediated cyclizations: Generality, scope, and mechanism. *J. Am. Chem. Soc.* **2002**, *124*, 2233–2244; (c) Nicolaou, K. C.; Montagnon, T.; Baran, P. S.; Zhong, Y. L. Iodine(V) reagents in organic synthesis, part 4: *o*-iodoxybenzoic acid as a chemospecific tool for single electron transfer–based oxidation processes. *J. Am. Chem. Soc.* **2002**, *124*, 2245–2258.
5. Ozanne, A.; Pouysegu, L.; Depernet, D.; Francois, B.; Quideau, S. A stabilized formulation of IBX (SIBX) for safe oxidation reactions including a new oxidative demethylation of phenolic methyl aryl ethers. *Org. Lett.* **2003**, *5*, 2903–2906.
6. Zhang, D.; Wu, L. Z.; Yang, Q. Z.; Li, X. H.; Zhang, L. P.; Tung, C. H. Versatile photosensitization system for $^1O_2$-mediated oxidation of alkenes based on Nafion-supported platinum (IT) terpyridyl acetylide complex. *Org. Lett.* **2003**, *5*, 3221–3224.
7. Recent reviews on ionic liquids: (a) Welton, T. Room-temperature ionic liquids: Solvents for synthesis and catalysis. *Chem. Rev.* **1999**, *99*, 2071–2083; (b) Wasserscheid, P.; Keim, W. Ionic liquids—New "solutions" for transition metal catalysis. *Angew. Chem., Int. Ed. Engl.* **2000**, *39* (21), 3772–3789.
8. Olivier, B. H. Ionic liquids: Perspectives for organic and catalytic reactions. *J. Mol. Catal. A* **2002**, *182–183*, 419–437.
9. Karthikeyan, G.; Perumal, P. T. An ionic liquid–mediated efficient oxidation of alcohols using o-iodoxybenzoic acid (IBX): A simple and eco-friendly protocol. *Synlett* **2003**, *14*, 2249–2254.
10. Chhikara, B. S.; Chandra, R.; Tandon, V. IBX in an ionic liquid: Eco-friendly oxidation of 17α-methylandrostan-3β,17β-diol, an intermediate in the synthesis of anabolic oxandrolone. *Tetrahedron Lett.* **2004**, *45*, 7585–7588.