# H<sub>2</sub>O<sub>2</sub>/Phosphonium Ionic Liquid: An Efficient and Simple Approach for Benzyl Halides Oxidation

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**Abstract:** An efficient oxidation of benzyl halide has been done using aqueous hydrogen peroxide (30%) in trihexyl(tetradecyl)phosphonium-tetrafluroborate ionic liquid the protocol is simple mild offering excellent yield of product.

Keywords: Benzyl halides, carbonyl compounds, aq. hydrogen peroxide (30%), ionic liquids.

# INTRODUCTION

Benzyl halides oxidation is an important tool in synthetic organic chemistry. Different reagents have been used for this transformation [1, 2]. In last 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 versatile oxidizing agent [4], because of its mild, selective, efficient and eco-friendly properties and operational simplicity. Oxygen mediated oxidation of alkenes using Nafion supported Platinum (II) Terpyridyl Acetylide complex is also used in Photosensitization reaction [5].

Non-volatile ionic liquids have been recognized as environmentally benign alternatives to volatile organic solvents [6]. They possess high thermal stability and good solvating ability. These ionic liquids not only work as solvent, but also enhance the rate of the reactions as like of catalyst. Products formed in these reactions are recovered by liquid-liquid extraction process [7]. Recently the oxidation of alcohols and diols has been reported using imidazoliun ionic liquids [8,9], peroxovanadate [10] and IBX [11], molecular Iodine/H<sub>2</sub>O<sub>2</sub>[12], H<sub>2</sub>O<sub>2</sub>/nitrile using Mg/Al hydrotalcite [13]. Hydrotalcite-supported SnO<sub>2</sub> catalyst was found to be effective in BV oxidations with hydrogen peroxide [14]. However; all these procedures are associated with certain limitations like long reaction time, hazardous conditions, poor yield, high temperature, etc. Thus, the introduction of new method for the oxidation of benzyl halides is still in high demand.

In the continuation of our work, we report a new environment friendly method for the oxidation of benzyl halide to corresponding carbonyl compounds (Scheme 1). The reaction completed in short time, affording the product in excellent yield. The results showed, method is compatible to the reported methods. Herein, we wish to report benzyl halide oxidation to corresponding carbonyl compounds using aq. hydrogen peroxide (30%) in the presence of phosphonium ionic liquid trihexyl(tetradecyl)phosphoniumtetrafluroborate [PhosIL-BF<sub>4</sub>].



Scheme 1.

# **POSSIBLE MECHANISM**

Step 1



Step 2



# **RESULT AND DISCUSSION**

Phosphonium ionic liquids (ILs) are highly basic in nature [15]. The general formula of these ionic liquids is

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 $[PR_3R']$  X, where both R and R' are alkyl groups and X is halide [16]. Their large radius and polarizable lone pair makes them more nucleophilic. The structural formula of ionic liquid trihexyl(tetradecyl)phosphonium-tetrafluroborate [PhosIL-BF<sub>4</sub>] is as shown in Fig. (1).



**Fig. (1).** Structure of trihexyl (tetradecyl) phosphonium-tetrafluroborate [PhosIL-BF<sub>4</sub>].

Phosphonium salts are thermally stable than ammonium salts. Phosphonium-based ionic liquids have higher viscosities than the ammonium counterparts at room temperature. However, on heating at 70-100 <sup>O</sup>C, their viscosities generally decrease. Whereas, the addition of reactants or catalysts further reduces the viscosity [17].

Oxidation of benzyl halides has been done using (30%) aq. H<sub>2</sub>O<sub>2</sub> as an oxidizing agent. The reaction carried out in water medium shows avoidance of the hazardous organic solvents which not only reduces the cost of the product but also is helpful for environmental safety. In this transformation we used "trihexyl (tetradecyl) phosphoniumtetrafluroborate [PhosIL-BF<sub>4</sub>]" as a phosphonium ionic liquid. Advantages of the use of phosphonium ionic liquid are 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 a slight change in its efficiency (0.5-1%). trihexyl(tetradecyl)phosphonium-tetrafluroborate [PhosIL-BF<sub>4</sub>] ionic liquid is less dense than water. Thus, just by decanting the aqueous streams the product is separated. In addition, the imidazolium ionic liquids are slightly acidic, which may result in carbene formation. However, the phosphonium ionic liquids do not possess any acidic proton, so no carbene formation takes place. Hence 100% utility of this ionic liquid can be achieved in organic transformations. Oxidation of non-substituted benzyl halide is completed in short time. However, the oxidation of substituted benzyl halide requires somewhat longer time. Electron rich substituted benzyl halide rates of oxidation were found to be higher as compared to electron poor substituted benzyl halides.

The product formation in this process is excellent 85-92 % (Table 1).

# GENERAL PROCEDURE OF BENZALDEHYDE SYNTHESIS

A mixture of benzyl bromide (1 mmol.), (30%) aq. hydrogen peroxide (30%) (3 mmol.), trihexyl (tetradecyl) phosphonium-tetrafluroborate [PhosIL-BF<sub>4</sub>] (1 ml.) was stirred at 50  $^{\circ}$ C temperature under nitrogen atmosphere for appropriate time. After completion of reaction as confirmed on thin layer chromatography (TLC), 25 ml. distilled water was added. The mixture was extracted with ethyl acetate solvent (3 x 10ml). Solvent ethyl acetate 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 <sup>o</sup>C temperatures to remove the water and the residual ionic liquid was recycled and reused for several times without any change in their efficiency (Table 2).

# SPECTRAL DATA

<sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded at room temperature on a varian Inova Spectrometer in CDCl<sub>3</sub> using TMS as internal standard.

# **3-Hydroxy-4-methoxy benzaldehyde (3c)**

<sup>1</sup>*H NMR* (*CDCl*<sub>3</sub>): δ 3.8 (s, 3H, OCH<sub>3</sub>), 6.2 (s, 1H, OH), 6.8 (dd, 1H, Ar-H), 7.5 (s, 1H, Ar-H), 7.4 (dd, 1H, Ar-H), 9.8 (s, 1H, CHO). <sup>13</sup>*C* (*CDCl*<sub>3</sub>): 56.4 (1C, OCH<sub>3</sub>), 112.1 (1C, Ar), 113.5 (1C, Ar), 125.1 (1C, Ar), 130.8 (1C, Ar), 146.2 (1C, Ar), 152.3 (1C, Ar), 191.2 (1C, CHO).

# 3-Nitro benzaldehyde (3f)

<sup>1</sup>*H* NMR (*CDCl*<sub>3</sub>):  $\delta$  7.6 (dd, 1H, Ar-H), 7.8 (dd, 1H, Ar-H), 7.9 (dd, 1H, Ar-H), 8.2 (dd, 1H, Ar-H), 10.4 (s, 1H, CHO). <sup>13</sup>*C* (*CDCl*<sub>3</sub>): 123.7 (2C, Ar), 131.1 (2C, Ar), 139.9 (1C, Ar), 151.2 (1C, Ar), 190.5 (1C, CHO).

# 4-methoxybenzaldehyde (3i)

<sup>1</sup>*H NMR* (*CDCl*<sub>3</sub>): δ 3.7 (s, 3H, OCH<sub>3</sub>), 6.9 (dd, 2H, Ar-H), 7.7 (dd, 2H, Ar-H), 9.8 (s, 1H, CHO). <sup>13</sup>*C* (*CDCl*<sub>3</sub>): 56.0 (1C, OCH<sub>3</sub>), 115.2 (2C, Ar), 130.5 (2C, Ar), 127.2 (1C, Ar), 165.5 (1C, Ar), 191.5 (1C, CHO).

# 4-(benzyloxy)-3-methoxybenzaldehyde (3j)

<sup>1</sup>*H NMR* (*CDCl*<sub>3</sub>):  $\delta$  3.7(s, 3H, -OCH<sub>3</sub>), 7.2(s, 1H, Ar-H), 7.3(dd, 1H, Ar-H), 6.8(dd, 1H, Ar-H), 5.1(s, 2H, -OCH<sub>2</sub>), 7.1(s, 5H, Ar-H), 9.8(s, 1H, CHO). <sup>13</sup>*C* (*CDCl*<sub>3</sub>): 56.3 (1C, OCH<sub>3</sub>), 150.5 (1C, Ar), 115.2 (1C, Ar), 130.5 (1C, Ar), 123.1 (1C, Ar), 115.7 (1C, Ar), 155.7 (1C, Ar), 71.3(1C, -CH<sub>2</sub>-Ar), 141.5(1C, Ar), 127.1(2C, Ar), 129.1(2C, Ar), 127.5(1C, Ar), 191.1 (1C, CHO).

# 3,4-dimethoxybenzaldehyde (3b)

<sup>1</sup>*H NMR* (*CDCl*<sub>3</sub>): δ 3.8 (s, 6H, -OCH<sub>3</sub>), 7.2 (s, 1H, Ar-H), 6.9 (dd, 1H, Ar-H), 7.1(dd, 1H, Ar-H), 9.9 (s, 1H, -CH0).

#### 3,4-bis(benzyloxy)benzaldehyde (3d)

<sup>1</sup>*H NMR* (*CDCl*<sub>3</sub>): δ 7.1 (s, 10H, Ar-H), 5.2 (s, 4H, -OCH<sub>2</sub>), 7.2 (s, 1H, Ar-H), 6.9 (dd, 1H, Ar-H), 7.1 (dd, 1H, Ar-H), 9.7 (s, 1H, -CHO).

#### 4-Nitro benzaldehyde (3e)

<sup>1</sup>*H NMR* (*CDCl*<sub>3</sub>): δ 8.0 (dd, 2H, Ar-H), 8.9 (dd, 2H, Ar-H), 9.9 (s, 1H, -CHO).

# Table 1. Conversion of Aryl Halides to Carbonyl Compounds in Ionic Liquid

Entries	Substrate (1)	(30%) aq. H <sub>2</sub> O <sub>2</sub> (Eq.) (2)	) (2) Yield (%) Time (Min)		Products (3)	
a	Br	3	90	17	ОН	
b	MeO OMe	3	89	40	MeO OMe	
с	MeO OH Br	3	88	50	MeO OH	
d	BnO OBn	3	90	30	BnO OBn	
e	O <sub>2</sub> N Br	3	92	55	O <sub>2</sub> N H	
f	Br NO <sub>2</sub>	3	87	60	NO <sub>2</sub>	
g	BnO	3	86	30	BnO	
h	O <sub>2</sub> N Br	3	87	120	O <sub>2</sub> N H	
i	MeO	3	85	160	MeO H	
j	MeO OBn	3	92	230	CHO MeO OBn	

Table 2. Recovery of Ionic Liquid in Carbonyl Compound Synthesis

Entry	Aryl Halide	Product	Time(min)	Yield(%) of Recovered Ionic Liquid			
				Cycle 1	Recycle 1	Recycle 2	
1	1a	3a	17	90	89	88	
2	1b	3b	40	89	87	87	

# 4-(benzyloxy)benzaldehyde (3g)

<sup>1</sup>*H NMR* (*CDCl*<sub>3</sub>): δ 7.1 (s, 5H, Ar-H), 6.9 (dd, 2H, Ar-H), 7.8 (dd, 2H, Ar-H), 5.1 (s, 2H, -OCH<sub>2</sub>), 9.8 (s, 1H, -CHO).

#### 4-Nitrobenzene-1,2-dialdehyde (3h)

<sup>1</sup>*H NMR* (*CDCl*<sub>3</sub>): δ 8.7 (s, 1H, Ar-H), 8.5 (dd, 1H, Ar-H), 8.1(dd, 1H, Ar-H), 10.25 (s, 2H, -CHO).

# CONCLUSIONS

In summary we demonstrated an efficient and mild protocol for the selective oxidation of benzyl halides to corresponding aldehydes using aq. hydrogen peroxide (30%) as an agent in the presence of phosphonium ionic liquid. The method offers several advantages such as high yields, shorter reaction time, cleaner reaction profiles and simple experimental and work up procedure.

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#### REFERENCES

- Chandrasekhar, S.; Sridhar, M. A. bifunctional approach towards the mild oxidation of organic halides: 2- dimethylamino-N, Ndimethylaniline 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.
- 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. Engl.*, 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. Engl., 2001, 40, 2812. 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 routs to heterocyclic compounds via o-iodoxybenzoic acidmediated 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] Zhang, D.; Wu, L. Z.; Yang, Q. Z.; Li, X. H.; Zhang, L. P.; Tung, C. H. Versatile photosensitization system for 1O2-mediated oxidation of alkenes based on Nation-supported platinum (IT) terpyridyl acetylide complex. *Org. Lett.*, **2003**, *5*, 3221-3224.
- [6] 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 liquidsnew "solutions" for transition metal catalysis. *Angew. Chem. Int. Ed. Engl.*, **2000**, *21*, 3772-3789.
- [7] Olivier-Bourbigoub, H. Ionic liquids: perspectives for organic and catalytic reactions. J. Mol. Catal. A, 2002, 182-183, 419-437.
- [8] 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.
- [9] 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.
- [10] Li, C.; Zheng, P.; Li, J.; Zhang, H.; Cui, Y.; Shao, Q.; Ji, X.; Zhang, J.; Zhao, P.; Xu, Y. The dual roles of oxodiperoxovanadate both as a nucleophile and an oxidant in the green oxidation of benzyl alcohols or benzyl halides to aldehydes and ketones. *Angew.Chem. Int. Ed. Engl.*, **2003**, *42*, 5063-5066.
- [11] Moorthy, J. N.; Singhal, N.; Senapati, K. Oxidations with IBX: benzyl halides to carbonyl compounds, and the one-pot conversion of olefins to 1,2-diketones. *Tetrahedron Lett.*, 2006, 47, 1757-1761.
- [12] Gaikwad, D. D.; Dake, S. A.; Kulkarni, R. S.; Jadhav, W. N.; Kakde, S. B.; Pawar, R. P. Efficient baeyer-villiger oxidation of ketones using molecular iodine/H2O2 as heterogeneous catalytic system. *Syn. Commun.*, **2007**, *37*, 4093-4097.
- [13] Llamas, R. Sanchidrian, C. J.; Ruiz, J. R. Heterogeneous Baeyer-Villiger oxidation of ketones with H<sub>2</sub>O<sub>2</sub>/nitrile, using Mg/Al hydrotalcite as catalyst. *Tetrahedron*, 2007, 63, 1435-1439.
- [14] Pillai, U. R.; Sahle-Demessie, E. Sn-exchanged hydrotalcites as catalysts for clean and selective Baeyer–Villiger oxidation of ketones using hydrogen peroxide. J. Mol. Catal. A: Chem., 2003, 191, 93-100.
- [15] Taramatee, R.; Daisuke, D. I.; Jason, A. C. Phosphonium ionic liquids as reaction media for strong bases. *Chem. Commun.*, 2005, 325-327.
- [16] Rosonkiewicz, A. C.; Pernak, J.; Feder J. K.; Ramani, A.; Robertson A. J.; Seddon, K. R. Synthesis, anti-microbial activities and anti-electrostatic properties of phosphonium-based ionic liquids. *Green Chem.*, 2005, 7, 855-862.
- a) Wolff, M. O.; Alexander, K. M.; Belder, G. Uses of quaternary phosphonium compounds in phase transfer catalysis. *Chim. Oggi.*, 2000, 18, 29-32. b) Seddon, R.; Stark, A.; Torres, M. Influence of chloride, water, and organic solvents on the physical properties of ionic liquids. *J. Pure Appl. Chem.*, 2000, 72, 2275-2287.