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# Selective oxidation of primary alcohols to aldehydes with $H_5IO_6/V_2O_5$ in ionic liquid

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## Abstract

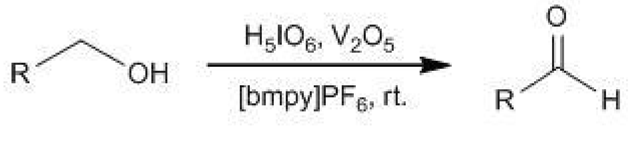
An efficient protocol for the selective oxidation of primary alcohols to aldehydes with $H_5IO_6/V_2O_5$ in ionic liquid [bmpy][$PF_6$] has been developed. High yields of the products, mild reaction conditions and simple experimental procedure make this protocol complementary to the existing methods. The catalyst can be reused for several times without obvious loss of the catalytic activity.

***Keywords:*** Oxidation; Primary alcohol; Aldehyde; Ionic liquid; Catalyst.

## 1. Introduction

The Oxidation of primary alcohols to the corresponding aldehydes is one of the most important transformations in organic synthesis [1, 2]. Recently, many methods for the oxidation of alcohols have been reported and variety of reagents such as tungsten [3], permanganate [4], bromate [5], palladium [6, 7], ruthenium [8], manganese [9], rhenium [10], copper [11], and iron [12] have been reported for this reaction. However, the search for the new readily available and green methods is still being actively pursued.

Recently, ionic liquids have attracted extensive interest as green media in organic synthesis due to their favorable properties. As a class of potential greener solvents, ionic liquids exhibit many unique physicochemical properties, such as negligible volatility and nonflammability under ambient conditions, large liquid range, high thermal stability, wide electrochemical window, and strong ability to dissolve many chemicals [13, 14]. Jacques Muzart summarized the oxidation methods of organic compounds carried out in the presence of ionic liquids [15]. In continuation of our interest in exploring green oxidation in ionic liquids [16], we herein report an selective oxidation of primary alcohols to aldehydes with $H_5IO_6/V_2O_5$ in ionic liquid [bmpy][$PF_6$] (Scheme 1).



**Scheme 1** Oxidation of primary alcohols to aldehydes.

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## 2. Experimental Section

### 2.1. Materials and Methods

All starting chemicals (AR grade) were purchased from commercial suppliers and some chemicals were further purified by recrystallization or distillation. Melting points were determined on a Thomas Hoover capillary apparatus and were uncorrected. The IR spectra were recorded with a Bomem Michelson model 102 FTIR. $^1$H NMR spectra were recorded on Bruker DRX (500 MHz) spectrometer. Elemental analyses were performed on a Yanagimoto MT3CHN recorder. The ionic liquids were synthesized according to the literature procedures [16, 17].

### 2.2. Experimental procedures

Alcohol (10 mmol), ionic liquid [bmpy]$PF_6$ (5 mL), $V_2O_5$ (0.3mmol) and $H_5IO_6$ (12 mmol) were added to a two-necked 50 mL round-bottomed flask. The reaction mixture was vigorously stirred at room temperature for the appropriate time. After the reaction, a two-layer mixture was obtained (organic phase/water phase). The reaction was monitored using TLC. After completion of the reaction, the product was extracted with dichloromethane. The solvent was removed and the residue was distilled under vacuum to give the desired product. The rest of ionic liquid and the catalyst were recovered by concentration under vacuum. Fresh substrates were then recharged to the recovered catalyst system and then recycled under identical reaction conditions. The products were identified by $^1$H NMR, IR data and physical data (mp) by comparison with literature data.

## 3. Results and Discussion

In the initial experiments, different ionic liquids were screened for the oxidation of primary alcohols. Herein the oxidation of benzyl alcohol was selected to be the model. The results are summarized in Table 1. It was shown that the reactions could proceed effectively in ionic liquids. It was observed that [bmpy]$PF_6$ demonstrated the best performance, providing a 92% high yield. In the absence of the ionic liquids, the reaction proceeded sluggishly. Obviously, the catalyst $V_2O_5$ is an essential component of the reaction.

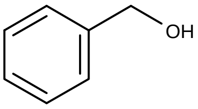
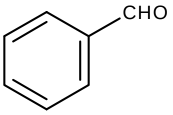
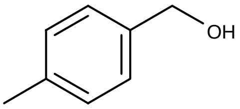
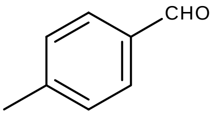
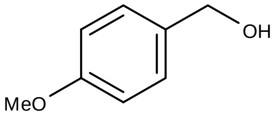
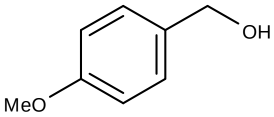
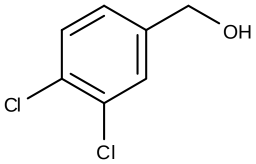
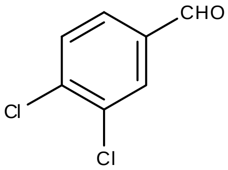
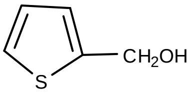
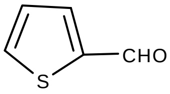
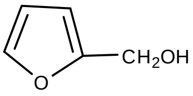
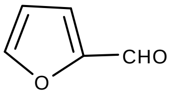
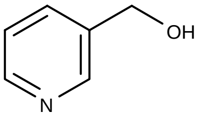
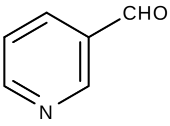
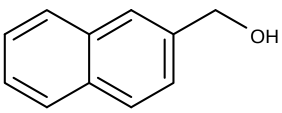
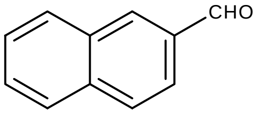
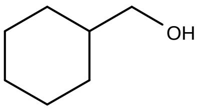
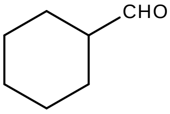
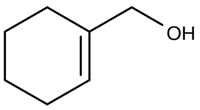
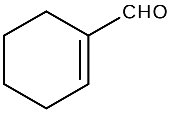
**Table 1**
Conditions for oxidizing benzyl alcohol in ionic liquids [a].

| Entry | Ionic liquid | Catalyst | Time (h) | Yield (%) [b] |
|---|---|---|---|---|
| 1 | [bmin]$BF_4$ | $V_2O_5$ | 6 | 76 |
| 2 | [hmim]$PF_6$ | $V_2O_5$ | 6 | 80 |
| 3 | [bpy]$PF_6$ | $V_2O_5$ | 6 | 82 |
| 4 | [bmpy]$PF_6$ | $V_2O_5$ | 6 | 92 |
| 5 | [bmpy]$PF_6$ | - | 6 | 52 |
| 6 | - | $V_2O_5$ | 6 | 58 |

[a] Benzyl alcohol (10mmol), ionic liquid (5mL), $V_2O_5$ (0.3mmol) and $H_5IO_6$ (12mmol)
[b] Isolated yield

With these results in hand we decided to explore the scope of this method. The oxidation of a variety of substituted primary alcohols in the presence of [bmpy]$PF_6$ was conducted and the obtained results are summarized in Table 2. It can be seen that the oxidation of a variety of substituted primary alcohols in the presence of [bmpy]$PF_6$ proceeded smoothly to give the corresponding products in high yields. Compared to the classical method, one additional important feature of the present protocol is the ability to tolerate variation in all components simultaneously. Compare with traditional solvents, ionic liquids are easily reused, which is superior to the conventional solvents and catalysts. When optimizing the reaction condition, the recycling performance of [bmpy]$PF_6$ in the same model reaction was investigated. The catalyst and ionic liquid could be reused at least five times without significant decrease in catalytic activity (Fig. 1).

**Table 2**
Oxidation of different alcohols [a].

| Entry | Substrate | Product | Time (h) | Yield (%) [b] |
|---|---|---|---|---|
| 1 |  |  | 6 | 92 |
| 2 |  |  | 7 | 93 |
| 3 |  |  | 4 | 90 |
| 4 |  |  | 8 | 92 |
| 5 |  |  | 8 | 85 |
| 6 |  |  | 6 | 88 |
| 7 |  |  | 8 | 83 |
| 8 |  |  | 16 | 90 |
| 9 |  |  | 4 | 94 |
| 10 |  |  | 4 | 91 |

[a] All products were characterized by IR, $^1H$ NMR, and their mp were in comparison with that of previous literatures. [b] Isolated yield.

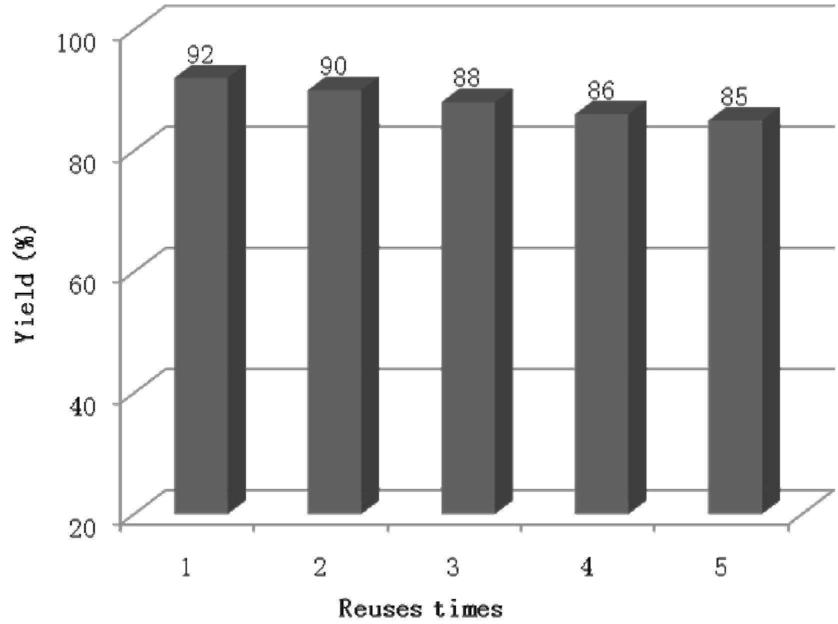
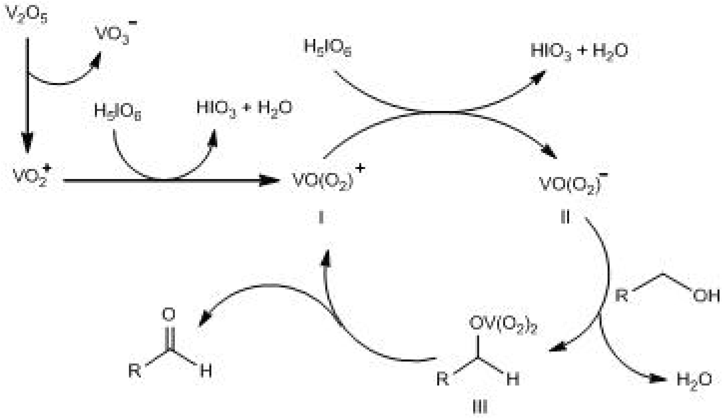


**Fig. 1.** Reusability of [bmpy]$PF_6$ and catalyst.

The mechanism for the oxidation of various alcohols to aldehydes using the catalyst has been proposed by comparison with the literature reports [16, 17]. In acidic solution, $V_2O_5$ can exist as $VO_2^+$ and $VO_3^-$ at first. Addition of $H_5IO_6$ to $VO_2^+$ can give the red oxoperoxo $VO(O_2)^+$ (I) and the yellow oxodiperoxo $VO(O_2)_2^-$ species (II), and then , III eliminated the oxoperoxo (I) to yield the desired product (Scheme 2).



**Scheme 2** Possible mechanism of alcohols oxidation.

## 4. Conclusion

In conclusion, we have described an efficient protocol for the oxidation of primary alcohols to aldehydes with $H_5IO_6/V_2O_5$ in ionic liquid [bmpy][$PF_6$]. High yields of the products, mild reaction conditions and simple experimental procedure make this protocol complementary to the existing methods. Further, the catalyst can be reused without obvious loss of the catalytic activity.

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