Catalysis Communications 11 (2010) 923–927

Contents lists available at ScienceDirect

Catalysis Communications

journal homepage: www.elsevier.com/locate/catcom

Highly efficient oxidation of organic halides to aldehydes and ketones with H_5IO_6 in ionic liquid $[C_{12}mim][FeCl_4]$

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ARTICLE INFO

Article history:
Received 4 March 2010
Received in revised form 28 March 2010
Accepted 29 March 2010
Available online 7 April 2010

Keywords:
Oxidation
Organic halide
H_5IO_6
Ionic liquid

ABSTRACT

A simple, mild, and efficient procedure for the oxidation of organic halides to aldehydes and ketones with H_5IO_6 in ionic liquid $[C_{12}mim][FeCl_4]$ has been developed. The oxidation reactions afford the target products in good to high yields and no overoxidation was observed. The products can be separated by a simple extraction with organic solvent, and the catalytic system can be recycled and reused without loss of catalytic activity.

1. Introduction

Aldehydes and ketones are important classes of chemicals used extensively for the preparation of a variety of fine or special chemicals such as drugs, vitamins, fragrances, etc. [1], and versatile methods for direct conversion of halides to these compounds have been reported [2]. The Hass–Bender [3] and Sommelet reactions [4] are two well-known methods for such a conversion. While the former method is only satisfactory for *para*-substituted benzylic substrates, the latter unfortunately has limited substrate scope. Oxidation with dimethyl sulfoxide (DMSO) [5,6], amine oxides [7], pyridine *N*-oxides [8], *N*-alkoxypyridinium salts [9,10], polymer supported reagents [11], pyrazinyl sulfoxides [12], $NaIO_4$-DMF [13], IBX [14], dimethyl selenoxide [15], H_2O_2 [16] and other reagents [17–20] has also been reported. However, some of the procedures are invariably associated with one or more disadvantages such as long reaction times, high temperatures, low yields, difficulties in work up, environmental hazards, etc. Oxidation of benzyl halides to their corresponding aldehydes and ketones with potassium nitrate catalyzed by phase transfer catalyst in aqueous media is another method, which was developed by our group [21], but, the procedure still suffered from harsh reaction conditions and separation difficulties. Consequently, there is a great need to develop new and environmentally-benign procedures that address all the drawbacks.

Ionic liquids (ILs) steadily gain wide recognition as environmentally-benign solvents because of their favourable 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 [22]. Therefore, ILs have been widely studied for many applications in chemical synthesis [23–25], biocatalytic transformations [26,27], electrochemistry [28], and analytical and separation science [29,30].

In continuation of our interest in exploring green oxidations in ionic liquids, we report herein a new and efficient method for the selective oxidation of organic halides to aldehydes or ketones with H_5IO_6 in ionic liquid 1-dodecyl-3-methylimidazolium iron chloride ($[C_{12}mim][FeCl_4]$) under mild conditions (Scheme 1). Furthermore, we demonstrate that the catalytic system can be recycled and reused without any significant loss of catalytic activity.

2. Experimental

2.1. General

All the chemicals were of analytical grade, purchased from commercial sources and used without further purification. The ionic liquids were synthesized according to the literature procedure [31]. Melting points were recorded on a Buchi R-535 apparatus and are uncorrected. ^1H NMR spectra were recorded on a Bruker 400-MHz spectrometer using $CDCl_3$ as the solvent with tetramethylsilane (TMS) as an internal standard. Elemental analysis was performed on a Vario EL III instrument (Elmentar Analysen Systeme GmbH, Germany).

2.2. General procedure for the oxidation of organic halides

To a stirred solution of organic halide (10 mmol) in $[C_{12}mim][FeCl_4]$ (0.4 mmol) was added H_5IO_6 (11 mmol) and then stirring was

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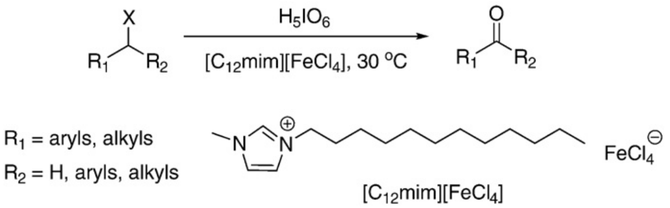
doi:10.1016/j.catcom.2010.03.017



Scheme 1. Oxidation of organic halides to aldehydes and ketones in [C_{12}mim][$FeCl_4$].

Table 1
Optimization of the reaction conditions for oxidizing benzyl chloride to benzaldehyde.[a]

Entry	Ionic liquid	Ionic liquid/equiv.	Time/h	Yield/%[b]
1	[C_{12}mim][$FeCl_4$]	–	4	42
2	[C_{12}mim][$FeCl_4$]	0.01	3	68
3	[C_{12}mim][$FeCl_4$]	0.03	2	92
4	[C_{12}mim][$FeCl_4$]	0.04	2	94
5	[C_{12}mim][$FeCl_4$]	0.05	2	94
6	[C_{12}mim][$FeCl_4$]	0.04	2	94[c]
7	[C_{12}mim][$FeCl_4$]	0.04	2	93[d]
8	[C_{12}mim][$FeCl_4$]	0.04	2	93[e]
9	[C_4mim][$FeCl_4$]	0.04	2	75
10	[C_6mim][$FeCl_4$]	0.04	2	78
11	[C_8mim][$FeCl_4$]	0.04	2	83
12	[C_{10}mim][$FeCl_4$]	0.04	2	91

[a] Reaction conditions: benzyl chloride (10 mmol), H_5IO_6 (11 mmol), 30 °C.
[b] Isolated yield.
[c] The first run.
[d] The second run.
[e] The third run.

continued at 30 °C for an appropriate time, the reaction progress was monitored by TLC. Upon completion, the reaction mixture was extracted with dichloromethane (3×10 mL). The dichloromethane solution was washed with 5% $NaHCO_3$ and dried over anhydrous Na_2SO_4. The product was purified by distillation (liquid product) or recrystallization from ethyl acetate and hexane (solid product). The product was characterized by ^{1}H NMR and elemental analysis. The recovered catalytic system was then recycled under identical reaction conditions. Spectroscopic data of the selected products are as follows.

2.2.1. *4-Tert-butylbenzaldehyde* (**5**)

Colorless oil. ^{1}H NMR: δ 1.32 (s, CH_3, 9H), 7.51–7.77 (m, Ar–H, 4H), 9.94 (s, CHO, 1H). Anal. Calcd. for $C_{11}H_{14}O$: C, 81.44; H, 8.70; O, 9.86. Found: C, 81.37; H, 8.70; O, 9.84.

2.2.2. *2,4,6-Trimethylbenzaldehyde* (**6**)

Colorless oil. ^{1}H NMR: δ 2.17 (s, CH_3, 3H), 2.42 (s, CH_3, 6H), 7.23 (s, Ar–H, 2H), 9.91 (s, CHO, 1H). Anal. Calcd. for $C_{10}H_{12}O$: C, 81.04; H, 8.16; O, 10.80. Found: C, 81.02; H, 8.16; O, 10.78.

2.2.3. *3,4,5-Trimethoxybenzaldehyde* (**7**)

White solid, mp: 74–76 °C. ^{1}H NMR: δ 3.76 (s, CH_3O, 3H), 3.91 (s, CH_3O, 6H), 7.12–7.17 (s, Ar–H, 2H), 9.85 (s, CHO, 1H). Anal. Calcd for $C_{10}H_{12}O_4$: C, 61.22; H, 6.16; O, 32.62. Found: C, 61.19; H, 6.17; O, 32.63.

2.2.4. *3,4-Methylenedioxybenzaldehyde* (**8**)

White solid, mp: 36–38 °C. ^{1}H NMR: δ 6.05 (s, CH_2, 2H), 6.85–7.54 (m, Ar–H, 3H), 9.87 (s, CHO, 1H). Anal. Calcd for $C_8H_6O_3$: C, 64.00; H, 4.03; O, 31.97. Found: C, 63.99; H, 4.01; O, 31.98.

2.2.5. *3,7-Dimethyl-2,6-octadienal* (**12**)

Colorless liquid. ^{1}H NMR: δ 1.57 (s, CH_3, 3H), 1.91 (s, CH_3, 3H), 2.23 (s, CH_3, 3H), 2.61 (m, CH_2CH_2, 4H), 5.10 (s, CH, 1H), 5.85 (d, $J=7.0$ Hz, CH, 1H), 9.80 (d, $J=7.0$ Hz, CHO, 1H). Anal. Calcd for $C_{10}H_{16}O$: C, 78.90; H, 10.59; O, 10.51. Found: C, 78.88; H, 10.59; O, 10.50.

2.2.6. *4-Nitrobenzaldehyde* (**15**)

Light yellow solid, mp: 104–106 °C. ^{1}H NMR: δ 8.12–8.34 (m, Ar–H, 4H), 10.24 (s, CHO, 1H). Anal. Calcd for $C_7H_5NO_3$: C, 55.63; H, 3.33; N, 9.27; O, 31.76. Found: C, 55.60; H, 3.34; N, 9.26; O, 31.78.

2.2.7. *Cinnamaldehyde* (**16**)

Colorless oil. ^{1}H NMR: δ 6.64 (d, $J=16.7$ Hz, CH, 1H), 6.71 (dd, $J=6.5$, 16.7 Hz, CH, 1H), 7.36–7.51 (m, Ar–H, 5H), 9.65 (d, $J=6.5$ Hz, CHO, 1H). Anal. Calcd for C_9H_8O: C, 81.79; H, 6.10; O, 12.11. Found: C, 81.75; H, 6.11; O, 12.13.

3. Results and discussion

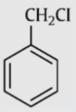
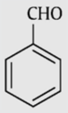
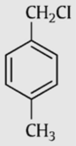
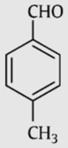
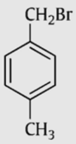
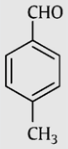
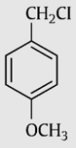
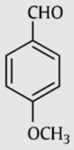
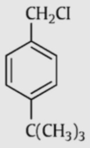
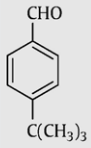
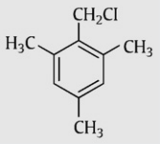
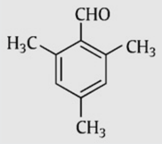
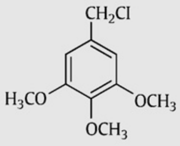
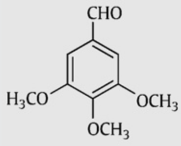
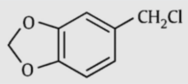
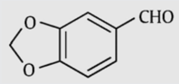
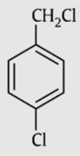
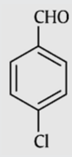
The initial study was carried out using benzyl chloride as the substrate to optimize the reaction conditions, and the results are summarized in Table 1. At first, the oxidation was tested with H_5IO_6 as the oxidant in the presence and absence of [C_{12}mim][$FeCl_4$]. In the absence of [C_{12}mim][$FeCl_4$], the reaction proceeded very slowly, and the yield was only 42% after 4 h (Table 1, entry 1). When the reaction was performed with [C_{12}mim][$FeCl_4$], the yield increased to 68% in a shorter time (3 h) when only 0.01 equivalents were used (Table 1, entry 2). The yield improved with increasing amount of [C_{12}mim][$FeCl_4$] (Table 1, entries 2–4), and reached maximum with 0.04 equivalents of [C_{12}mim][$FeCl_4$] (Table 1, entry 4). However, further addition of [C_{12}mim][$FeCl_4$], under the same conditions, did not enhance significantly the yield (Table 1, entry 5). These experiments revealed that 2 h and 0.04 equivalents of the promoter were necessary to complete the reaction. In addition, the IL could be typically recovered and reused for subsequent reactions with no appreciable decrease in yields and reaction rates (Table 1, entries 6–8). Besides [C_{12}mim][$FeCl_4$], four other types of ionic liquids, 1-butyl-3-methylimidazolium iron chloride ([C_4mim][$FeCl_4$]), 1-hexyl-3-methylimidazolium iron chloride ([C_6mim][$FeCl_4$]), 1-methyl-3-octylimidazolium iron chloride ([C_8mim][$FeCl_4$]), and 1-decyl-3-methylimidazolium iron chloride ([C_{10}mim][$FeCl_4$]) were tested as catalysts in the reaction (Table 1, entries 9–12). [C_{12}mim][$FeCl_4$] demonstrated the best performance. The different catalytic effects of ILs may be attributed to their different abilities of stabilizing and dissolving H_5IO_6 and the substrate. Under reaction conditions, H_5IO_6 may be more soluble in [C_{12}mim][$FeCl_4$], leading to higher effective concentration of the oxidant. The reaction procedure apparently did not result in the oxidation of benzaldehyde since no benzoic acid was detected.

With these results in hand, we subjected other organic halides to the oxidation reactions, and the results are listed in Table 2. It is clear that various types of benzylic, allylic, and aliphatic halides, both primary and secondary, can be successfully oxidized to the corresponding aldehydes and ketones in good to high yields (Table 2). Various functionalities such as alkyl, alkoxy, alkene double bonds, fluoro, chloro and nitro groups can tolerate the reaction. However, aliphatic halides were less reactive, and longer reaction time was needed to reach good yields (Table 2, entries 17 and 18). It was also observed that the electronic nature of the substituents on the aromatic ring has some impact on the reaction rate. Substrates with electron-withdrawing groups (Table 2, entries 9, 10, and 15) are less reactive than the ones with electron-donating groups (Table 2, entries 2–8).

4. Conclusions

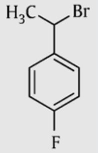
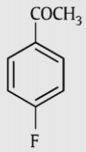
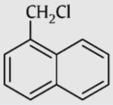
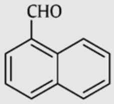
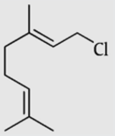
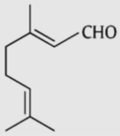
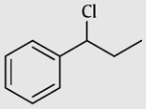
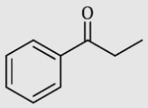
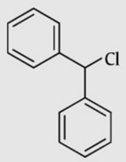
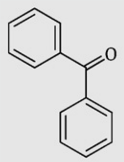
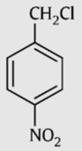
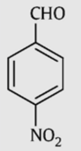
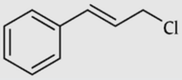
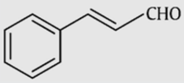
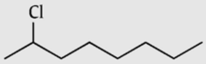
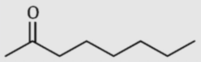
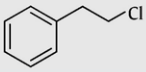
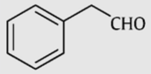
In conclusion, we have developed a simple and efficient procedure for the oxidation of organic halides to aldehydes and ketones with H_5IO_6 in ionic liquid [C_{12}mim][$FeCl_4$]. Most importantly, the catalytic system is very easy to handle and can be recycled and reused without loss of catalytic activity. The scope, the definition of mechanism, and synthetic applications of the oxidation are currently under investigation.

Table 2
Oxidation of organic halides to aldehydes and ketones.[a]

Entry	Substrate	Product	Time/h	Yield/%[b]
1		 **1**	2	94
2		 **2**	1.5	93
3		 **3**	1.5	93
4		 **4**	1.5	95
5		 **5**	1.5	96
6		 **6**	1.5	98
7		 **7**	1.5	98
8		 **8**	1.5	95
9		 **9**	2	92

(continued on next page)

Table 2 (*continued*)

Entry	Substrate	Product	Time/h	Yield/%[b]
10		 **10**	2.5	91
11		 **11**	1.5	97
12		 **12**	2	96
13		 **13**	2	93
14		 **14**	2.5	95
15		 **15**	2.5	90
16		 **16**	2	94
17		 **17**	3	88
18		 **18**	3	90

[a] Reaction conditions: organic halide (10 mmol), H_5IO_6 (11 mmol), [C_{12}mim][$FeCl_4$] (0.4 mmol), 30 °C.

[b] Isolated yield.

Acknowledgements

We thank the National Basic Research Program (973) of China and Natural Science Foundation of Jiangsu Province for support of this research.

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