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Chinese Chemical Letters 23 (2012) 801–804

CHINESE CHEMICAL LETTERS

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Oxidation of alcohols to aldehydes and ketones using selenium ionic liquid

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Received 15 March 2012
Available online 9 June 2012

Abstract

A new type of ionic liquid supported selenium reagents were synthesized and found to be an excellent catalyst in the oxidation of alcohols to aldehydes and ketones in the presence of 30% H_2O_2. The predictable solubility of ionic liquids allows an easy separation of the oxidation products from the reaction mixture. Furthermore, the oxidation reaction can be carried out using an ionic liquid as the solvent, and the ionic liquid-supported selenium reagents can be recycled and used for four times with a little decrease in catalytic performance.

Keywords: Selenium ionic liquids; Aldehydes; Ketones; Oxidation

The oxidation of alcohols into the corresponding aldehydes and ketones is a fundamental and pivotal class of chemical transformations and is extensively used in both laboratory and industry [1,2]. In spite of their great prevalence, these processes are not without drawbacks; they can implicate expensive reagents, large amount of waste, and tedious purifications. Excellent transition-metal catalysts, based on, *e.g.*, Cu, Pd, Ru, and Pt, have been developed which allow the use of molecular oxygen as the terminal oxidant [3]. However, these metal catalysts are often unsuitable for highly functionalized molecules which are used as intermediates in the pharmaceutical industry. Although new oxidation methods have been developed over the past decades [4], novel methods permitting the oxidation reaction in a simple and environmentally benign fashion to carry out these transformations are still highly desirable because of the importance of the oxidative processes as well as the development of greener methodologies.

On the other hand, organoselenium chemistry has been developed rapidly over the past decades, and selenium-based methodology is a powerful tool in organic synthesis now [5,6]. Selenium dioxide is widely used as a selective and valuable oxidant. However, these reactions suffer a serious disadvantage of the formation of colloidal selenium, being difficult to remove from the reaction mixture. These problems can be overcome by use of organoselenium compounds. Selenoxide as a co-oxidant could oxidize alcohol to aldehydes by adding catalytic equivalent of selenium dioxide in refluxed dioxane for 1 day [7]. But organic selenides are highly malodorous and generally unpleasant, and difficult to handle with [8], especially the toxicity. These properties have reduced their attractiveness for applications.

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http://dx.doi.org/10.1016/j.cclet.2012.05.019

Ionic liquids have received much attention in recent years as environmentally benign reaction media for organic synthesis [9]. They possess many interesting properties such as wide liquid range, negligible vapor pressure, high thermal stability and high loading capacity. They have also been refereed to as ‘‘designable solvents’’ because their chemical and physical properties can be adjusted by modifying the structure of the cation or the anion.

Thus, we aim to render the organoselenium compounds non-volatile, easily recoverable and recyclable by anchoring the selenium function to the ionic liquid moiety, and to study the use of selenium ionic liquid as a solvent and catalyst in the oxidation of alcohols to aldehydes and ketones.

1. Results and discussion

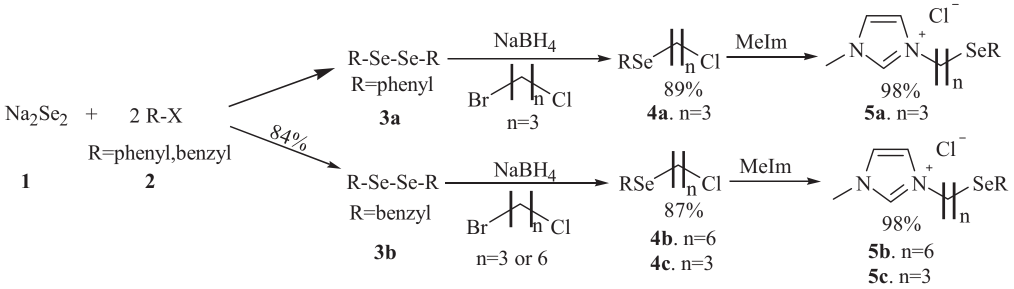
The details of the preparation of the ionic liquids were outlined in Scheme 1. As shown in Scheme 1, the preparation of the ionic liquid-supported selenium compounds started from Na_2Se_2 **1** and aryl halide **2** (Scheme 1). The diaryl diselenides **3b** (this compound was synthesized following the literature procedure [10]) were formed in 84% yield (**3a** yield only 17%) by simple extraction using dichloromethane. The arylselenide anion ($ArSe^-$) was readily prepared by reduction of **3** with $NaBH_4$, followed by reaction with chloralkane bromide gave the selenide compound **4** in 87% yield. The reactivity of halides ranked in the order Br > Cl. The following substitution by *N*-methylimidazol led to the ionic liquid-grafted selenium **5** at 80 °C in 98% yield with no need of chromatographic purification of intermediates and there was no foul smell released in any of the operations. All new ionic liquids described in this paper were characterized by ^1H, ^{13}C NMR and mass spectrum.

Following our previous work, the catalyst **5a**, however, proved to be difficult to prepare. Therefore, **5b** was chosen as a more suitable precursor of the same active species. We decided to explore the utility of the new ionic liquid **5b** in the alcohol oxidation reaction. Initially, we chose benzyl alcohol as a substrate to screen the optimized conditions for the reaction in the presence of 1.0 mL of **5b** (1.35 g, 4.1 mmol). After extensive trials and errors (Table 1), higher temperature and longer reaction time had positive effects on the conversion rate of benzyl alcohol. It should be mentioned that further increasing of the reaction temperature was followed by a reduction in the conversion rate of benzyl alcohol (Table 1, entry 5), owing to the oxidative decomposition of Se catalyst. (At higher temperatures, the *syn*-elimination reaction occurs [11].) High amount of oxidant had also negative effects on the conversion rate of benzyl alcohol (Table 1, entry 9), we found that facile β-elimination have occurred leading to the fragmentation of the imidazolium moiety from the selenoxides (Scheme 2). Ionic liquid **5c** also had been completed to test (entry 11), the result is not good, β-elimination have also occurred leading to the fragmentation of the imidazolium moiety from the selenoxides.

The optimal conditions consisted of 1 equiv. of benzyl alcohol as substrates and 1.0 mL of **5b** as solvent and catalyst, 8.2 mmol of H_2O_2 as oxidant at 60 °C for 1 day, and no over-oxidation products are observed even after extended reaction times (Table 1, entry 8).

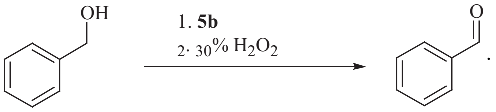
Under these conditions, a variety of alcohols were oxidized into the corresponding carbonyl compounds in moderate to good yields. The electron-withdrawing group decreased the reaction yields such as 4-nitrobenzyl alcohol gave *p*-nitrobenzaldehyde in only 32% yield (entry 1). Furthermore the reactivity of the secondary benzylic alcohols was affected by R substituent groups probably due to the steric hindrance, and moderate yields were attained (Table 2). Allylic alcohols are more readily oxidized than other alcohols (entries 3 and 10). The extension of this catalytic system to the oxidation of saturated aliphatic alcohols was examined (entry 11), and achieve better result.

In addition, a study regarding the recovering and reusing of the ionic liquid was also performed. After the full conversion, the product was extracted with petroleum ether, the inferior, ionic liquid phase was dried under vacuum



Scheme 1. Preparation of ionic liquid-grafted selenium.

Table 1
Oxidation conditions of benzyl alcohol.

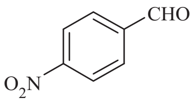
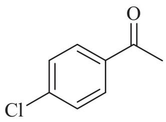
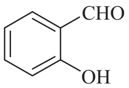
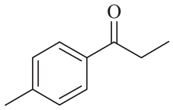
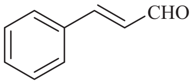
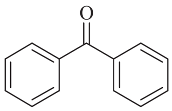
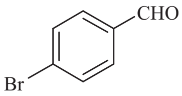
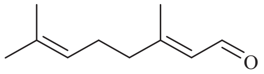
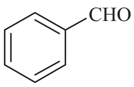
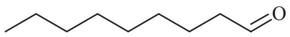
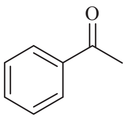


Entry	T (°C)	Time (h)	Molar ratio [a]	Product yield [b]
1	25	4	0:1	0%
2	25	4	1:1	15%
3	40	4	1:1	20%
4	60	4	1:1	24%
5	80	4	1:1	19%
6	60	12	1:1	41%
7	60	24	1:1	51%
8	60	24	1:1.5	53%
9	60	24	1:2	67%
10	60	24	1:4	60%

[a] Molar ratio: 5b/hydrogen peroxide.

[b] Yields are given for pure isolated products. 6-phenyl-1-hexene was found as byproduct.

Table 2
Oxidation of several alcohols.

Entry[a]	Product	Yield[b] (%)	Entry[a]	Product	Yield[b] (%)
1		32	7		43
2		62	8		47
3		65	9		51
4		61	10		57
5		(1) 59[c] (2) 56[d] (3) 57[e]	11		41
6		49			

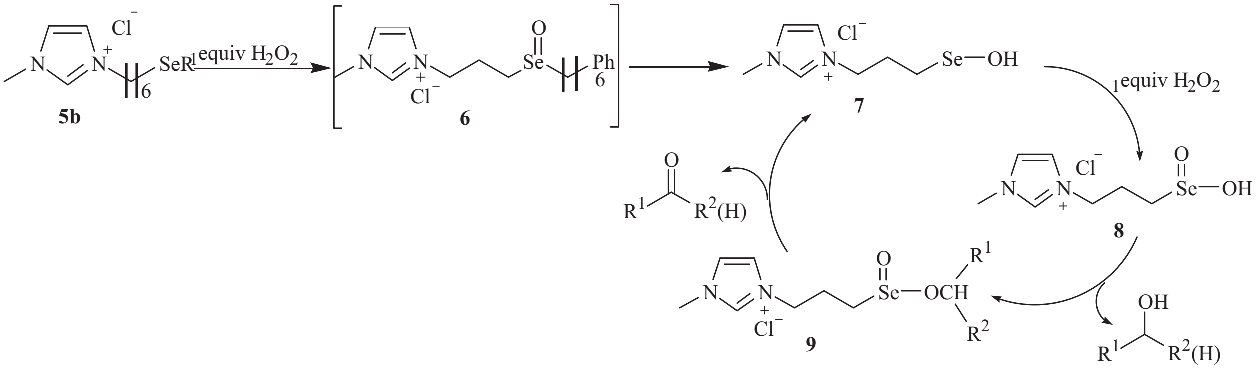
[a] Reaction performed on a 1 mmol scale.

[b] Yields are given for pure isolated products.

[c] The second run after Table 1, entry 9.

[d] The third run after entry 5 (**1**).

[e] The fourth run after entry 5 (**2**).



Scheme 2. Proposed catalytic cycle.

and reused. The selenium ionic liquid maintained its good level of oxidation activity even after being recycled four times as shown in Table 2, entry 5.

Although we have found no evidence for the generation of selenoxide **7**, there appear to be one possible routes for the formation of the aldehydes as outlined in Scheme 2. The oxidation of the selenide **5b** with 1 equiv. H_2O_2 generated the selenenic acid **7** [12a], and then the selenenic acid **7** oxidations with another 1 equiv. H_2O_2 gave the corresponding selenenic acid **8** and byproduct of 6-phenyl-1-hexene. And then react with alcohols *via* the formation of intermediate seleninate ester **9**. This type of intermediate has been proposed in several oxidation reactions to form aldehydes [12].

In summary, we have shown that the ionic liquid-supported selenium reagent **5b** could be easily prepared, and that **5b** could be used in oxidation reactions in an ionic liquid medium, affording carbonyl compounds in moderate to good yields. Additional advantages of **5b** are: easy to handle, environmentally benign, and easy recovery and recycling, although the scope of this reaction was somewhat narrow. Further investigations on developing more active selenium reagents and the mechanism for the oxidation of alcohols are now in progress.

Acknowledgment

This research was financially supported by National Science Foundation of Zhejiang province of China (No. Y404358).

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