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Publication details, including instructions for authors and subscription information: <u>http://www.tandfonline.com/loi/gpss20</u>

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To cite this article: Fengshou Tian, Yahong Chen, Peng Li & Shiwei Lu (2014) A Novel Method for Synthesis of 1, 3-Dialkylimidazole-2-Selenones in Water, Phosphorus, Sulfur, and Silicon and the Related Elements, 189:9, 1391-1395, DOI: <u>10.1080/10426507.2013.865124</u>

To link to this article: <u>http://dx.doi.org/10.1080/10426507.2013.865124</u>

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A NOVEL METHOD FOR SYNTHESIS OF 1, 3-DIALKYLIMIDAZOLE-2-SELENONES IN WATER

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GRAPHICAL ABSTRACT



Abstract A novel method for the synthesis of 1, 3-dialkylimidazole-2-selenones is described. The reaction of 1, 3-dialkylimidazolium salts with selenium using Na_2CO_3 as a base in water under refluxing conditions afforded 1, 3-dialkylimidazole-2-selenones in yields up to 95%.

Keywords 1, 3-Dialkylimidazolium salts; 1, 3-dialkylimidazole-2-selenones; Selenium; Water

INTRODUCTION

The chemistry of N-heterocyclic carbenes and their metal complexes^{1,2} is of considerable current interest duo to their applications in homogeneous catalysis³ and medicinal chemistry.⁴ Among them, 1, 3-dialkylimidazole-2-selenones are a type of chalcogen derivative of N-heterocyclic carbenes, and they are useful precursors for the synthesis of various N,Se-containing heterocycles.⁵ 1, 3-dialkylimidazole-2-selenones had been synthesized by reacting the corresponding iodide salts with selenium powder in methanol in the presence of potassium carbonate.⁶ 1, 3-dialkylimidazolium salts reacted with selenium in strong bases such as KH or NaH to give the corresponding 1, 3-dialkylimidazole-2-selenones.⁷ In addition, 1, 3-dialkylimidazolium salts also reacted with Na₂Se₂ in the presence of potassium *tert*-butoxide to afford the target products at room temperature in dry THF.⁸ Both Roy⁹ and Guziec¹⁰ reported that treatment of imidazole with BuLi and selenium power also gave 1, 3-dialkylimidazole-2-selenones under Schlenk conditions. However, most of the known methods for the preparation of imidazole-2-selenones suffer from disadvantages such as

Received 17 August 2013; accepted 6 November 2013.

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the use of strong bases and harsh reaction conditions, long reaction time, low yields, or complicated manipulations.

RESULTS AND DISCUSSION

In the course of our ongoing studies on organic selenium chemistry,¹¹ we found the 1, 3-dialkylimidazole-2-selenones catalyzed carbonylation of organic amines and ethanolamine using carbon monoxide as oxidant agents to give ureas and 2-oxazolidinone.¹² Keeping these results in mind, we investigated reactions of 1, 3-dialkylimidazolium salts with selenium in the presence of Na₂CO₃ in water under refluxing conditions and surprisingly found these reactions easily led to 1, 3-dialkylimidazole-2-selenones. Herein, we report a novel method for the synthesis of 1, 3-dialkylimidazole-2-selenones in the presence of Na₂CO₃ (Scheme 1).



Scheme 1

1-butyl-3-methylimidazolium chloride was treated with an equivalent of selenium in the presence of two equivalents of sodium carbonate in H_2O under refluxing condition for 4 h to give 1-butyl-3-methylimidazole-2-selenone (**1b**) in 92% (entry 1 in Table 1). We investigated the effect of different bases under similar conditions and found Na₂CO₃ is the best additive reagent for this reaction (entries 1–6 in Table 1). In addition, when two equivalents of Na₂CO₃ were used, the reaction yield was the highest (entries7–10 in Table 1).

Reactions of other 1, 3-dialkylimidazolium salts were also investigated and the results are summarized in Table 2. From Table 2, we can see that 1, 3-dialkylimidazolium

Entry ^a	Base	The ratio of amount of base and substrate	Yield ^b	
1	Na ₂ CO ₃	2:1	92	
2	K_2CO_3	2:1	91	
3	NaOAc	2:1	trace	
4	Et ₃ N	2:1	<3	
5	NaHCO ₃	2:1	7	
6	KHCO ₃	2:1	9	
7	Na ₂ CO ₃	1:1	45	
8	Na ₂ CO ₃	1.5:1	81	
9	Na ₂ CO ₃	1.5:1	90 ^c	
10	Na ₂ CO ₃	2:1	92	

Table 1 Effect of different bases to the reaction in water

^aReaction conditions: 1-butyl-3-methylimidazolidine chloride 5 mmol; Se, 5 mmol; H₂O, 5 mL; Base 10 mmol; Refluxing, 4 h; ^bIsolated yields. ^cRefluxing, 6 h.

Entry ^a	R	Х	Cmpd	Yield (%) ^b
1	n-Butyl	Cl	1b	92 ¹²
2	n-Butyl	Ι	1b	86 ¹²
3	n-Butyl	BF_4	1b	74 ¹²
4	n-Propyl	Br	2b	81 ^{8b}
5	Ethyl	Br	3b	80 ^{8b}
6	n-Hexadecyl	Br	4b	95 ¹²
7	2-Bromobenzyl	Br	5b	93°
8	3-Chlorobenzyl	Cl	6b	90 ^c
9	Iso-propyl	Br	7b	42 ^{8b}
10	Methyl	Ι	8b	47 ^{8b}

Table 2 Synthesis of 1, 3-dialkylimidazole-2-selenones in water

^aReaction conditions: 1, 3-dialkylimidazolium salts, 5 mmol; Se, 5 mmol; H₂O, 5 mL; Na₂CO₃, 10 mmol; 4 h. ^bIsolated yields. ^cNovel products.

chlorides, bromides, and tetrafluoroborate can react with selenium easily to give the corresponding 1, 3-dialkylimidazole-2-selenones in water under refluxing conditions (entries 1–8 in Table 2). The effect of steric hindrance on the 3-position of the imidazole rings did not significantly influence the yields of the products (entries 6–8 in Table 2). When 1isopropyl-3-methylimidazolium bromide and 1, 3-dimethylimidazolium iodide were used as the substrate, the yields of selenation reactions were reduced rapidly to 42% and 47% (entries 9–10 in Table 2).

In analogy with the mechanism proposed for the reaction of 1, 3-dialkylimidazolium salts and Se,⁷ the possible mechanism for the reaction is shown in Figure 1. The formation of 1-butyl-3-methylimidazole-2-selenone (**1b**) may involve a two-step pathways: (1) deprotonation of 1-butyl-3-methylimidazolium chloride (**1a**) by Na₂CO₃ to give the N-heterocyclic carbene intermediate C in water and (2) reaction of intermediate C with selenium to produce 1-butyl-3-methylimidazole-2-selenone (**1b**).

In summary, in our work, we have found a new method for the synthesis of 1, 3-dialkylimidazole-2-selenones from 1, 3-dialkylimidazolium salts and selenium in the presence of Na_2CO_3 in H_2O under refluxing conditions.



Figure 1 Proposed pathway to 1, 3-dialkylimidazole-2-selenone (1b).

Experimental Procedure for the Synthesis of 1, 3-Dialkylimidazole-2-Selenones

In a 50-mL, two-necked flask, 1-butyl-3-methylimidazolium chloride (5 mmol), selenium (5 mmol), Na_2CO_3 (10 mmol), H_2O (5 mL), and a magnetic stirring bar were placed. Then, the reaction mixture was vigorous stirring under refluxing condition for 4 h. After the reaction was complete, and the resultant mixture was filtered, and the solvent evaporated under reduced pressure. Further purification by recrystallization or column chromatography on silica gel gave the pure product. All the products were characterized by NMR and HRMS. Detailed characterization of the previously known compounds from Table 2 are presented in the Supplemental Materials.

Data of Novel Products

1-(2-bromobenzyl)-3-methyl-1H-imidazole-2(3H)-selenone 5b: Mp.110–112°C, 1H NMR (400 MHz, CDCl₃): δ 3.72 (s, 3H, N-CH₃), 5.46 (s, 2H, N-CH₂), 6.82 (br, J = 2.4Hz, 1H, CH), 6.90 (br, J = 2.4Hz, 1H, CH), 7.19 (m, 2H, 2 × Ar-H), 7.27 (d, J = 4.4 Hz, 2H, 2 × Ar-H), 7.58 (d, J = 7.6Hz, Ar-H). 13C NMR (100 MHz, CDCl₃): δ 14.09,22.51, 26.53, 29.13, 29.68, 30.96, 31.75, 37.05, 49.98, 118.64, 119.71, 155.33 (C=Se). HRMS for C₁₁H₁₁N₂BrSe: (m/z) calcd 329.9271; found. 329.9279 [M]+.

1-(3-chlorobenzyl)-3-methyl-1H-imidazole-2(3H)-selenone 6b: Mp.97–98°C, 1H NMR (400 MHz, CDCl3): δ 3.70 (s, 3H, N-CH₃), 5.34 (s, 2H, N-CH₂), 6.66 (s, 1H, CH), 6.96 (s, 1H, CH), 7.22–7.27 (m, 3H, 3 × Ar-H), 7.30 (s, 1H, Ar-H). 13C NMR (100 MHz, CDCl₃): δ 30.77, 37.11, 52.15, 118.43, 120.40, 126.15, 127.85, 128.14, 129.97, 134.29, 137.44, 156.26(C=Se). HRMS for C₁₁H₁₁N₂ClSe: (m/z) calcd 285.9776; found. 285.9753 [M]+.

FUNDING

We are grateful to the Natural Science Foundation of Henan Province (No. 142102310365 and No. 132300410176) and the Doctor Start-up Foundation of Zhoukou Normal University (No. zksybscx201204) for financial support.

SUPPLEMENTAL MATERIAL

Supplementary data for this article can be accessed on the publisher's website, www.tandfonline.com/gpss

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