

# Synthesis of 2,5-disubstituted selenophenes employing $\text{Se}^0/\text{KOH}$ system in ionic liquids

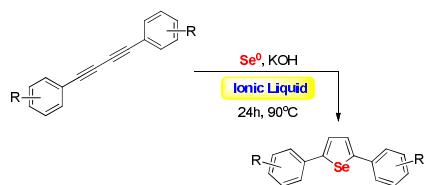
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## Introduction

Chalcogenophenes heterocycles (S, Se, Te) have numerous uses in biochemistry, physical organic chemistry, organic synthesis and materials chemistry.<sup>1</sup> These compounds have been studied intensively in recent years as organic materials.<sup>2</sup> However, as these technologies become commercialized, the active compounds will be required in larger amounts. Surprisingly the methods for their preparation are limited; multi-step synthesis, expensive reagents, harsh conditions, and thus their large scale application in industry is limited.<sup>3</sup> In the course of our research program dedicated to the development selenophene functional organic materials, we became interested in new methods for synthesis and functionalization of this molecular moiety.<sup>4</sup> Herein, an approach for harnessing the reactive  $\text{Se}^0/\text{KOH}$  system employing ionic liquid as polar recyclable solvent in a new methodology for 2,5-disubstituted selenophenes synthesis is reported (figure 1).



**Figure 1.** Synthesis of 2,5-disubstituted selenophenes employing ionic liquids.

## Results and Discussion

As already described, elemental chalcogens (Y = S, Se, Te) when treated with hydroxide bases undergoes a disproportionation giving the corresponding  $\text{Y}^{2-}$  nucleophiles.<sup>5</sup> In this sense, 1,4-diphenylbutadiyne (**1**) was used as electrophile to reach the suitable reaction conditions for selenophene (**2**) synthesis. Among solvents evaluated (table 1, entries 1-7), DMSO gave best results (entry 3). Additionally, by use of nonpolar solvent and 18-Crow-6 as additive, the yield of product **2** was increased (entry 7), suggesting the *in situ* formation of superbasic medium.<sup>6</sup> This system can furnish stronger bases and nucleophiles for elemental selenium disproportionation and nucleophilic addition of  $\text{Se}^{2-}$  species to triple bonds, respectively. Another bases were tested (entries 9-11), albeit KOH remains the best result (entry 3). Mild reaction conditions provide lower yield of

compound **2** (entry 12), and harsh conditions, such as elevated temperature and longer times did not improved the yields.

**Table 1.** Optimization of the reaction conditions.

Entry <sup>a</sup>	Solvent	Base	Temperature (°C)	Time (h)	Yield (%) <sup>b</sup>
1	DMF	KOH	90	24	28
2	MeCN	KOH	80	24	0
3	DMSO	KOH	90	24	70
4	DMSO	KOH	25	24	39
5	<i>i</i> -PrOH	KOH	82	24	35
6	EtOH	KOH	78	24	0
7	Toluene	KOH	90	24	0
8	Toluene	KOH/18-Crow-6 <sup>c</sup>	90	24	59
9	DMSO	NaOH	90	24	61
10	DMSO	<i>t</i> -BuOK	90	24	12
11	DMSO	NaH	90	24	14
12	DMSO	KOH	25	24	39
13	[BMMIm][NTf <sub>2</sub> ]	KOH	90	24	85

<sup>a</sup> 0.25 mmol of **1** / 3.0 equiv. of  $\text{Se}^0$  / 6.0 equiv. of base, under argon atmosphere and deoxygenated solvents (7.5 mL); <sup>b</sup> isolated yields; <sup>c</sup> 20 mol%.

A remarkable raise of reaction yield was achieved in ionic liquids (IL) as solvent (entry 13) given polar nature of reaction. [BMMIm][NTf<sub>2</sub>] was the first choice to avoid N-heterocyclic carbene (NHC) formation under this basic reaction condition. Currently, we are working on the IL recyclability, and studying the IL effect on reaction yields, since this solvent could play a task-specific role.<sup>7</sup>

## Conclusions

In conclusion, we present here a general and easy method for the synthesis of 2,5-disubstituted selenophenes employing  $\text{Se}^0/\text{KOH}$  system, with ionic liquids remarkable raising reaction yield. The mechanistic studies and reaction scope are under evaluation.

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