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Graphical Abstract

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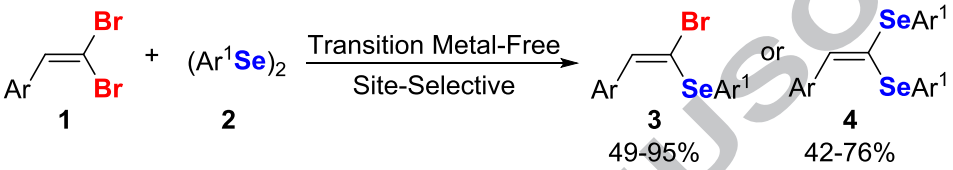

Ar = C_6H_5, 4-ClC_6H_4, 2-ClC_6H_4, 4-BrC_6H_4, 4-$CH_3C_6H_4$, 4-$CH_3OC_6H_4$, furyl

Ar^1 = C_6H_5, 4-FC_6H_4, 4-$CH_3OC_6H_4$

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1,1-Dibromoalkenes as versatile reagents to a transition metal-free and stereoselective synthesis of (*E*)-1-bromo-1-selenoalkenes and ketene selenoacetals

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ABSTRACT

We describe here a metal-free and selective method for the synthesis of (*E*)-1-bromo-1-seleno alkenes and ketene selenoacetals by a stoichiometric and temperature-controlled reaction. These protocols employ a diverse array of 1,1-dibromoalkenes and different diaryl diselenides to afford the corresponding products in good yields and in a short reaction time.

1. Introduction

Alkenes are unsaturated fragments ubiquitous in natural products and bioactive compounds and serve as key starting materials for innumerous chemical transformations.[1] The chemical behavior and the biological and pharmacological activities of the alkene are directly associated to the stereochemistry and substitution pattern of the double bond.[2] Considering an acyclic monoalkene, there are around ten different basic structural types with different substitution patterns.[3]

Therefore, the synthesis of stereodefined highly functionalized alkenes requires the use of selective and efficient methods. In 1962, Ramirez and co-workers presented a Witting-type procedure to prepare 1,1-dibromoalkenes from aldehydes.[4] Since then, several uses for these substrates have been reported in the literature. The use of 1,1-dibromoalkenes accompanied by transition-metal catalyzed reactions, specially palladium, nickel and copper, has made possible the stereoselective synthesis of several di- and trisubstituted alkenes.[5] Not only carbon–carbon bond has been formed, but also cross-coupling reactions using heteronucleophiles, such as nitrogen, oxygen, phosphorus, sulfur and selenium have been performed. Besides, 1,1-dibromoalkenes are starting materials for the preparation of internal alkynes and conjugated unsaturated bonds.[6] The synthesis of various *N*-, *O*-, and *S*-heterocycles has also been widely described, through a tandem cross-coupling/cyclization reaction, commonly catalyzed by copper and palladium salts.[7] Recently, (*E*,*E*)-1,3-dienyl bromides were used to prepare selanyl selenophenes under copper-catalyzed reaction[8] and 2-(2,2-dibromovinyl)phenol derivatives were the precursors of benzo[*b*]furans by a base-mediated metal-free preocedure.[9]

Although the versatility of 1,1-dibromoalkenes has been highly exploited and these methods are undeniably efficient, the use of stable, nontoxic, cheap and sustainable materials to site-selective synthesis is desired.[10] In this context, the transition metal-free mono- and di-bromo replacement of 1,1-dibromoalkenes by selenium species to generate selenoalkenes was not described so far.

Selenoalkenes are very important intermediates in organic synthesis and can be used as versatile building blocks for the construction of isolated or conjugated olefins.[11] Moreover, one of the main advantages of using selenoalkenes is the fact that these species can be readily transmetalated to generate the corresponding vinyl organometallics with retention of the double-bond geometry.[12] The importance of selenoalkenes is demonstrated also in the broad scope of their recent applications, including Negishi and Suzuki-type cross-coupling reactions,[13] the preparation of selenophenes[14] and *N*- and *O*-heterocycles,[15] among others. In this line, functionalized selenoalkenes, such as 1-bromo-1-selenoalkenes, are very interesting synthons in organic synthesis. The strategies for the synthesis of functionalized (*E*)-1-bromo-1-selenoalkenes use selenoalkynyl selenides as starting materials.[16] However, these methods suffer of the problems in using strong acids, toxic solvents, laborious synthesis of the starting materials and a mixture of (*E*)- and (*Z*)-isomers is obtained in most cases.

In this sense, we describe our results on the direct metal-free and regioselective synthesis of (*E*)-1-bromo-1-arylselanoalkenes **3** using diaryl diselenides **2** and 1,1-dibromoalkenes **1** as easily prepared starting materials. Moreover, a simple stoichiometric control also allowed obtaining the ketene selenoacetals **4** under mild reaction conditions (Scheme 1).[17]

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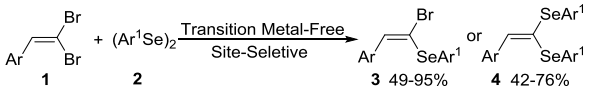


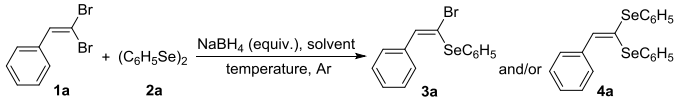
Ar = C_6H_5, 4-ClC_6H_4, 2-ClC_6H_4, 4-BrC_6H_4, 4-$CH_3C_6H_4$, 4-$CH_3OC_6H_4$, furyl

Ar^1 = C_6H_5, 4-FC_6H_4, 4-$CH_3OC_6H_4$

Scheme 1. General scheme of the reaction.

Initially, we chose 1,1-dibromoalkene **1a**, diphenyl diselenide **2a** and $NaBH_4$ as the standard starting materials to establish the best reaction conditions under argon atmosphere (Table 1). We examined temperature, amount of diphenyl diselenide, reducing agent, and the nature of the solvent.

Table 1. Optimization of reaction conditions.[a]



Entry	$(C_6H_5Se)_2$ **2a** (mmol)	Temp. (ºC)	Time (h)	Yield **3a** (%)[b]	Yield **4a** (%)[b]
1	0.25	25	18.0	41	traces
2	0.25	50	0.5	76	5
3	0.25	90	0.5	70	7
4	0.50	50	0.5	77	18
5[c,d]	**0.25**	**50**	**0.5**	**88**	**6**
6[e]	0.25	50	0.5	65	6
7[f]	0.25	50	4.0	-	-
8	0.60	90	2.0	6	68
9	**0.60**	**120**	**1.0**	**3**	**76**

[a]Reaction was performed with 1,1-dibromoalkene **1a** (0.5 mmol), diselenide **2a** and $NaBH_4$ (3.0 equiv. regarding to **2a**) in PEG-400 (2.0 mL) as solvent. [b]Yields are given for isolated products. [c]It was observed a lower than 1% yield of (*Z*)-isomer by GC/MS. [d]Reaction was performed using 1.0 mL of PEG-400. [e]Reaction was performed using $NaBH_4$ (2.0 equiv. regarding **2a**). [f]EtOH (1.0 mL) was used as solvent.

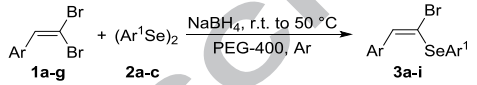
In our preliminary experiment, a mixture of 0.25 mmol of diphenyl diselenide **2a** and 0.75 mmol of $NaBH_4$ in PEG-400 (2.0 mL) was stirred at room temperature for 30 min under atmosphere of argon to afford *in situ* the nucleophilic selenium species. The diphenyl diselenide cleavage was accompanied by the change in the color of the reaction solution, from yellowish to colorless. After this, 1,1-dibromoalkene **1a** (0.5 mmol) was added in the reaction vessel and the reaction remained stirring at room temperature for an additional 18.0 h. Under these reaction conditions the desired product **3a** was obtained in 41% yield (Table 1, entry 1). Fortunately, when the same reaction was performed by gently heating (50 ºC), the yield of product **3a** increased to 76%, with the additional formation of the ketene selenoacetal **4a** in 5% yield (Table 1, entry 2). To our surprise, by increasing the temperature to 90 ºC, a decrease in the yield of the desired product **3a** to 70% was observed (Table 1, entry 3). When equimolar amounts of **1a** and **2a** were used at 50 ºC, compounds **3a** and **4a** were obtained in 77% and 18% yields, respectively (Table 1, entry 4). Gratefully, when the reaction was performed using 1.0 mL of PEG-400 at 50 ºC, the corresponding product (*E*)-1-bromo-1-phenylselanyl-2-phenylethene[16] **3a** was obtained in excellent 88% yield after 30 min (Table 1, entry 5). In another experiment, it was observed that by using 2.0 equiv. of $NaBH_4$ regarding to diselenide **2a**, the product **3a** was obtained in only 65% yield (Table 1, entry 6). When the nucleophilic selenium species were generated using EtOH as solvent, no products were obtained and a great amount of diphenyl diselenide **2a** and starting material **1a** was recovered (Table 1, entry 7). The use of a larger amount of diphenyl diselenide **2a** (0.6 mmol) at 90 or 120 ºC, significantly improved the selectivity to the formation of the ketene selenoacetal **4a** in 68% and 76% yield, respectively (Table 1, entries 8 and 9).

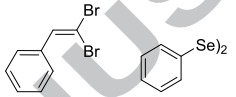
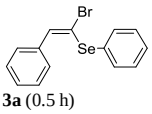
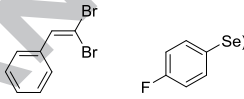
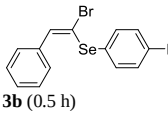
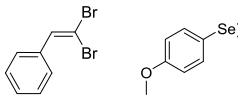
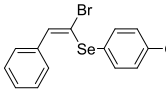
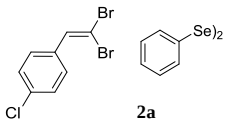
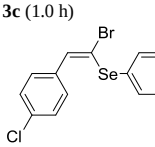
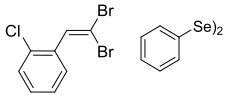
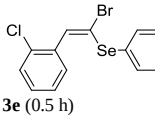
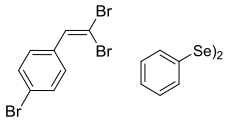
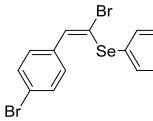
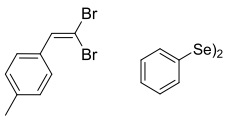
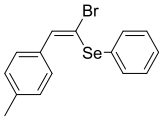
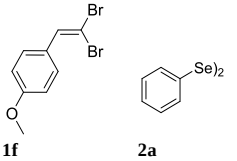
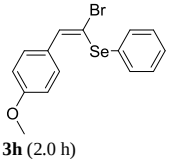
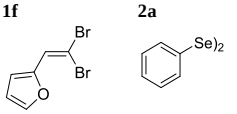
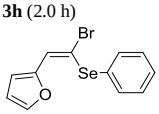
The experiments revealed that the selenation of 1,1-dibromoalkene **1a** to selective formation of (*E*)-1-bromo-1-phenylselenoalkene **3a** or ketene selenoacetal **4a** can be easily controlled by the temperature and the amount of diphenyl diselenide **2a**.

Based on the optimized reaction conditions showed in Table 1, we concluded that the best condition to prepare (*E*)-1-bromo-1-phenylselenoalkene **3a** is the use of 1,1-dibromoalkene **1a** (0.5 mmol) in combination with diphenyl diselenide **2a** (0.25 mmol) and $NaBH_4$ (0.75 mmol) in PEG-400 (1.0 mL) at 50 ºC for 30 min under argon (Table 1, entry 5).

In the next series of experiments, we studied the applicability of this reaction conditions to other 1,1-dibromoalkenes **1a-g** and diaryl diselenides **2a-2c**, and the results are showed in Table 2.

Table 2. Stereoselective synthesis of (*E*)-1-bromo-1-selenoalkenes **3a-i**.[a]



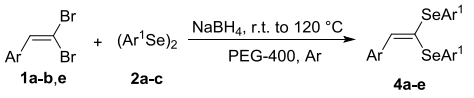
Entry	Alkene **1**	Diaryl Diselenide **2**	Product **3** (reaction time)	Yield (%)[b,c]
1	 **1a**	**2a**	 **3a** (0.5 h)	88
2	 **1a**	**2b**	 **3b** (0.5 h)	87
3	 **1a**	**2c**	 **3c** (1.0 h)	65
4	 **1b**	**2a**	 **3d** (0.5 h)	94
5	 **1c**	**2a**	 **3e** (0.5 h)	95
6	 **1d**	**2a**	 **3f** (0.5 h)	83
7[d]	 **1e**	**2a**	 **3g** (2.0 h)	63
8[d]	 **1f**	**2a**	 **3h** (2.0 h)	49
9	 **1g**	**2a**	 **3i** (2.0 h)	59

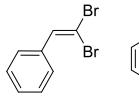
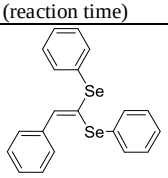
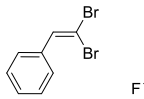
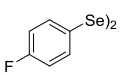
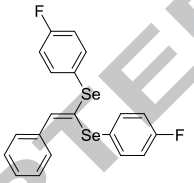
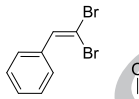
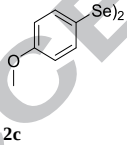
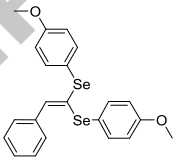
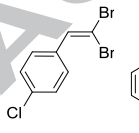
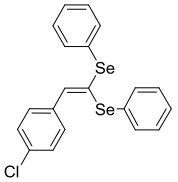
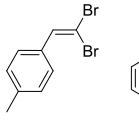
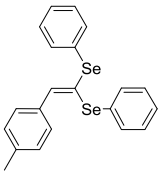
[a]Reaction was performed with 1,1-dibromoalkene **1** (0.5 mmol), diaryl diselenide **2** (0.25 mmol) and $NaBH_4$ (0.75 mmol) in PEG-400 (1.0 mL) as solvent at 50 ºC under argon. [b]Yields are given for isolated products. [c]It was observed a lower than 1% yield of (*Z*)-isomer by GC/MS. [d] Reaction was performed at 80 ºC.

As it can be seem in Table 2, the reaction showed high regio- and stereoselectivity in all the investigated cases. The reactions with 1,1-dibromoalkenes **1a-d**, bearing either neutral or electron-poor substituents in the aromatic ring, proceeded efficiently to afford the respective (*E*)-1-bromo-1-arylselenoalkenes **3a-f** in good yields and in short reaction times (Table 2, entries 1-6). The introduction of an electron-rich substituent in the aryl group of the 1,1-dibromoalkene **1**, as in **1e** and **1f**, gave the corresponding (*E*)-1-bromo-1-arylselenoalkenes **3g** and **3h** in 63% and 49% yield and a longer reaction time was needed for completion of the reaction (Table 2, entries 7 and 8). The reaction performed with the heteroaromatic 1,1-dibromo-2-furylethene **1g** furnished the respective product **3i** in 59 % yield (Table 2, entry 9).

On the other hand, it is important to mention that the reaction conditions [diphenyl diselenide **2a** (0.6 mmol) and PEG-400 at 120 °C] described in Table 1, entry 9, produced the ketene selenoacetal **4a**, corresponding to the incorporation of two arylselenyl units to 1,1-dibromoalkene **1a**. Thus, these findings prompted us to explore the possibility to develop a selective method to synthesize differently substituted ketene selenoacetals **4a-e** and the results are described in Table 3.

Table 3. Synthesis of ketene selenoacetals **4a-e**.[a]

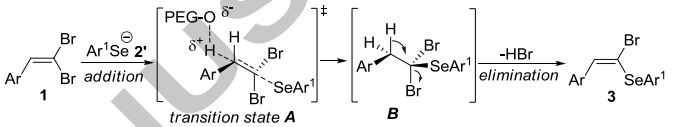


Entry	Alkene **1**	Diaryl Diselenide **2**	Product **4** (reaction time)	Yield (%)[b]
1	 **1a**	 **2a**	 **4a** (1.0 h)	76
2	 **1a**	 **2b**	 **4b** (1.0 h)	42
3	 **1a**	 **2c**	 **4c** (3.5 h)	55
4	 **1b**	 **2a**	 **4d** (1.0 h)	61
5	 **1e**	 **2a**	 **4e** (2.0 h)	65

[a]Reaction was performed with 1,1-dibromoalkene **1** (0.5 mmol), diaryl diselenide **2** (0.6 mmol) and $NaBH_4$ (1.8 mmol) in PEG-400 (2.0 mL) as solvent at 120 ºC under argon. [b]Yields are given for isolated products.

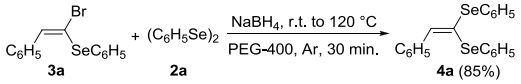
In this sense, we carried out the reactions employing diaryl diselenide **2a-c** containing electron neutral-, donating-, and withdrawing groups, and the products **4a-c** were obtained in satisfactory yields (Table 3, entries 1-3). To complete this investigation, 1,1-dibromoalkenes **1b** and **1e** reacted with diphenyl diselenide **2a**, and the corresponding products **4d** and **4e** were isolated in 61% and 65% yield, respectively (Table 3, entries 4 and 5).

A plausible mechanism for the reactions of 1,1-dibromoalkenes **1** with diaryl diselenides **2** using PEG-400 as solvent for formation of (*E*)-1-bromo-1-arylselenoalkenes **3** and ketene selenoacetals **4** is depicted on Scheme 2. At first, the saturated intermediate **B** is generated via addition of phenylselenolate **2'** to the double bond, with the involvement of the PEG-stabilized transition state **A**.[18] Then, elimination of HBr, through an anti-periplanar conformation results in the formation of the target product **3**.[19] The stereochemistry of product **3** was confirmed by a Br/Li exchange[20] (see support information). A similar mechanism could be involved in the formation of the ketene selenoacetal **4**, but with the addition of a second phenylselenyl group to **3**.



Scheme 2. The proposed reaction mechanism.

To prove this statement, we carried out the reaction of the (*E*)-1-bromo-1-arylselenoalkene **3a** with diphenyl diselenide **2a** under the optimized reaction conditions (Table 1, entry 9). After generated *in situ* the nucleophilic selenium specie, the alkene **3a** was added and the reaction mixture was maintained at 120 ºC for 30 minutes, giving the expected ketene selenoacetal **4a** in 85% yield (Scheme 3).



Scheme 3. Synthesis of ketene selenoacetal **4a** from **3a**.

In conclusion, we have developed an efficient and general transition metal-free method for the synthesis of (*E*)-1-bromo-1-arylselenoalkenes and ketene selenoacetals from readily available 1,1-dibromoalkenes. The chemoselectivity of the reaction we controlled by simple modification of the reaction conditions, adjusting parameters as stoichiometry and temperature. Finally, we envision great acceptance and applicability for these simple and practical procedures, which provide straightforward entries to highly valuable building blocks. Additionally, several studies are currently in development in our laboratory using 1,1-dibromoalkenes, which we intend to publish as full papers in the due course.

Acknowledgments

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17. **General procedure of the reaction of 1,1-dibromoalkenes with diaryl diselenides**: To a solution of diaryl diselenide **2** [0.25 mmol] in PEG-400 (1.0 mL) under Ar atmosphere, $NaBH_4$ (0.029 g, 0.75 mmol) was added at room temperature and the mixture was stirred for 30 min. Then, the 1,1-dibromoalkene **1** (0.5 mmol) was added and the temperature was slowly raised to 50 ºC. The reaction progress was monitored by TLC. After the time indicated in Table 2, the reaction mixture was quenched with water (10.0 mL) and extracted with ethyl acetate (3x 15.0 mL). The organic phase was separated, dried with $MgSO_4$ and the solvent was evaporated under reduced pressure. The product **3** was isolated by column chromatography using silica gel 60Å (0.060-0.200 mm-Across) and hexane as the eluent. For the synthesis of ketene selenoacetals **4**, the same methodology was used, except that 0.6 mmol of diaryl diselenide **2**, 2.0 mL of PEG-400 and 1.8 mmol of $NaBH_4$ were used to afford *in situ* the nucleophilic species of selenium and the system was stirred at 120 ºC for the time indicated in Table 3.
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Highlights

1,1-Dibromoalkenes as versatile reagents to synthesis of selenoalkenes

Metal-free and selective method for the synthesis of (*E*)-1-bromo-1-selenoalkenes

Metal-free and selective method for the synthesis of ketene selenoacetals