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Multicomponent reactions of allenes, diaryl diselenides, and nucleophiles in the presence of iodosobenzene diacetate: direct synthesis of 3-functionalized-2-arylselenyl substituted allyl derivatives

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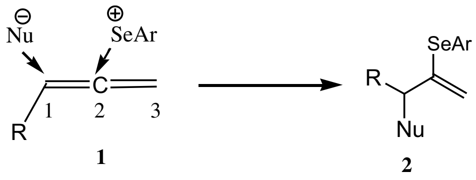
Abstract—A multicomponent reaction of allenes, diaryl diselenides, and nucleophiles in the presence of iodosobenzene diacetate has been developed, providing a novel method for the preparation of synthetically useful 3-functionalized-2-arylselenyl substituted allyl derivatives.

During the last decade, allenes have attracted much attention of chemists and have been widely investigated due to their higher reactivity than non-cumulated C–C double bonds. A variety of compounds could be synthesized with the employment of allenes.[1] Usually the reactions of allenes include ionic additions,[2] free radical additions,[3] transition metal catalyzed reactions[4] and so on.

The ionic additions of allenes provide allyl derivatives, which are important building blocks in transition metal catalyzed organic synthesis.[5] Selenium compounds are of great interest because of their synthetic applications[6] and biological activities such as antitumor, antibacterial activities, and other properties.[7] However, to the best of our knowledge, the direct synthesis of 3-functionalized-2-arylselenyl substituted allyl derivatives is not well documented in the literature.[8]

It is well known that arylselenyl cation can be generated from diaryl diselenide in the presence of oxidants and the addition of arylselenyl cations to C–C double bonds will produce β-arylselenyl substituted carbon cations, which can react with nucleophiles.[9] Thereby, we hypothesized that 3-functionalized-2-arylselenyl substituted allyl derivatives **2** could be prepared by the addition of arylselenyl cation to allenes, then followed by the trapping with nucleophiles on the double bond between C1 and C2 selectively (Scheme 1).

We initially examined the reaction of 1-phenyl allene **1a** and diphenyl diselenide in the presence of dibenzoyl peroxide in ethanol at reflux. After 12 h, the expected product 2-phenylselenyl-3-ethoxyl-3-phenyl-1-propylene was obtained in 33% yield (Table 1, entry 1). Further screening demonstrated that iodosobenzene diacetate was a better oxidant (Table 1, entry 3). The yield of **2a** increased at higher temperature (Table 1, entries 3 and 4). The employment of excess alcohol as solvent was necessary and the yield of **2a** decreased sharply when the reaction was carried out in other solvent such as chloroform (Fig. 1; Table 1, entry 5).



Scheme 1.

Keywords: Ionic addition; Allene; Allyl derivative; Selenium chemistry.

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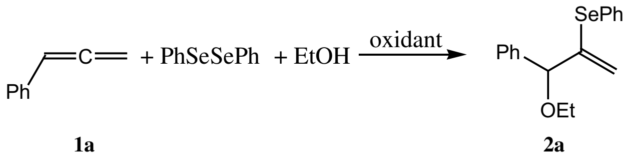
Table 1. Reaction of 1-phenyl allene, diphenyl diselenide and ethanol in the presence of oxidants[a]



Entry	Oxidant	Solvent	Temperature (°C)	Time[b] (h)	Yield[c] (%)
1	$(PhCO_2)_2$	EtOH	78	12	33
2	SeO_2	EtOH	78	14	0[d]
3	$PhI(OAc)_2$	EtOH	78	10	64
4	$PhI(OAc)_2$	EtOH	60	14	43
5	$PhI(OAc)_2$	$CHCl_3$[e]	60	16	15[f]

[a] Compound **1a** (0.3 mmol), diphenyl diselenide and oxidant, and 2 mL of solvent were used.

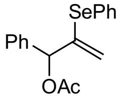
[b] The reaction was monitored by TLC (eluent: petroleum ether).

[c] Isolated yields.

[d] Compound **2a** was not observed but a series of unidentified compounds were obtained.

[e] Containing 0.6 mmol of EtOH.

[f] Besides **2a**, 31% of **2e** (Fig. 1) was obtained; the acetate anion came from iodosobenzene diacetate.



2e

Figure 1.

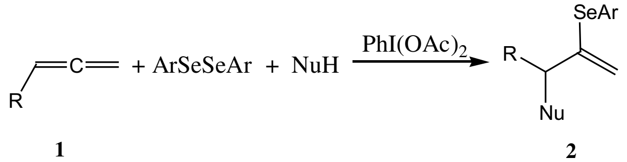
With these encouraging results in hand, a series of nucleophiles, diaryl diselenides, and allenes were employed to prepare the corresponding 3-functionalized-2-arylselenyl allyl derivatives (Table 2).[10]

It is obvious that the primary alcohols were easier to react with the α-arylselenyl substituted carbon cations and the yields of the corresponding 2-arylselenyl substituted allyl derivatives **2** were higher (Table 2, entries 1 and 2). When secondary or tertiary alcohols were employed, the yields of the products were lower (Table 2, entries 3 and 4), probably due to the steric hindrance. When carboxylic acids were employed, the corresponding 2-arylselenyl substituted allyl esters could also be obtained smoothly (Table 2, entries 5 and 6).

The 3-functionalized-2-arylselenyl allyl derivatives **2** were obtained smoothly when aryl substituted allenes were employed (Table 2, entries 8–11). However, when alkyl substituted allenes were employed, **3** were obtained instead of the expected products **2** (Scheme 2).

Here we propose a possible mechanism: the arylselenyl cation, generated from diaryl diselenide and iodosobenzene diacetate,[9] may add to allene **1** and form the arylselenyl substituted carbon cation **4**. When R is an aryl group, **4** could be well stabilized by the adjacent aryl group and the nucleophiles would attack the C1 carbon to produce the final product **2**. When R is an alkyl group, nucleophiles would attack the C3 carbon due to the lower steric hindrance. Thus, **3** would be produced (Scheme 3).

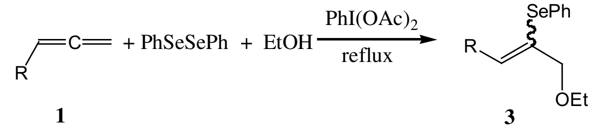
Table 2. Preparation of 3-functionalized-2-arylselenyl allyl derivatives[a]



Entry	R	Ar	NuH	Yield of **2**[b]
1	C_6H_5	C_6H_5	EtOH	**2a** (64)
2	C_6H_5	C_6H_5	CH_3OH	**2b** (62)
3	C_6H_5	C_6H_5	$(CH_3)_2CHOH$	**2c** (41)
4	C_6H_5	C_6H_5	$(CH_3)_3COH$	**2d** (28)
5	C_6H_5	C_6H_5	CH_3COOH	**2e** (71)
6	C_6H_5	C_6H_5	C_3H_7COOH	**2f** (61)
7	C_6H_5	*p*-MeC_6H_4	EtOH	**2g** (70)
8	*p*-MeC_6H_4	C_6H_5	EtOH	**2h** (61)
9	*o*-MeC_6H_4	C_6H_5	EtOH	**2i** (56)
10	2,6-$(CH_3)_2C_6H_3$	C_6H_5	EtOH	**2j** (47)
11	α-$C_{10}H_7$	C_6H_5	EtOH	**2k** (63)

[a] Compound **1** (0.3 mmol), diaryl diselenides and iodosobenzene diacetate, and 2 mL of NuH were used. The reaction was carried out at 100 °C when the boiling point of NuH was higher than 100 °C, otherwise, the reaction was carried out at reflux.

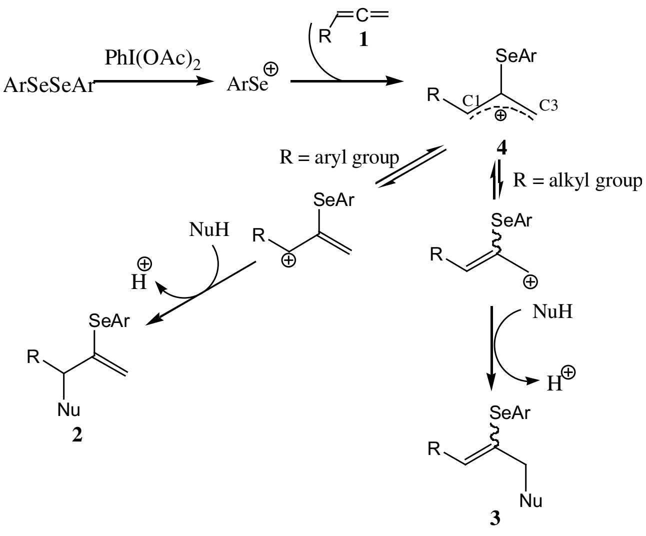
[b] Isolated yields.



1l: R = C_4H_9 **3l** 37% (Z/E = 1:1)

1m: R = $C_{12}H_{25}$ **3m** 31% (Z/E = 1:1)

Scheme 2.



Scheme 3.

In conclusion, we reported a facile synthesis of 3-functionalized-2-arylselenyl allyl derivatives via the multicomponent reaction of allenes, diaryl diselenides, and nucleophiles. The reaction mechanism and synthetic applications of this methodology are being further studied in our laboratory.

Acknowledgements

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Supplementary data

The relevant spectroscopic data of all the new compounds mentioned in the Letter are contained in the Supplementary data file. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2006.12.026.

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10. *2-Phenylselenyl-3-ethoxyl-3-phenyl-1-propylene* **2a**. *Typical procedure*: To the mixture of diphenyl diselenide (0.3 mmol, 94 mg) and iodosobenzene diacetate (0.3 mmol, 97 mg), a solution of 1-phenyl allene **1a** (0.3 mmol, 35 mg) in ethanol (2 mL) was added. The mixture was stirred at reflux and the reaction was monitored by TLC (eluent: petroleum ether). When the reaction was completed, the solvent was evaporated under vacuum, the residue was subjected to preparative TLC (eluent: petroleum ether) to afford **2a** (61 mg, 64%).

    Selected data of **2a**: Yellow oil. ^{1}H NMR (400 Hz, CDCl$_3$): δ 7.22–7.54 (m, 10H), 5.73 (s, 1H), 5.11 (s, 1H), 4.91 (s, 1H), 3.43–3.60 (m, 2H), 1.24 (t, $J = 6.8$ Hz, 3H). ^{13}C NMR (100 Hz, CDCl$_3$): δ 15.2, 64.7, 84.6, 116.3, 127.1, 127.8, 128.0, 128.2, 128.5, 129.2, 135.5, 140.0, 145.6. IR (Film, cm^{-1}): 3059, 2974, 1475, 1441, 1094, 740, 695. MS (70 eV, EI) *m/z*: 318 (M$^+$, 21), 317 (M$^+$$-$1, 12), 274 (31), 135 (100).