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Ring-opening reactions of arylvinylidenecyclopropanes with diaryl diselenide upon heating: formation of 1,2-diarylselenocyclopentene derivatives

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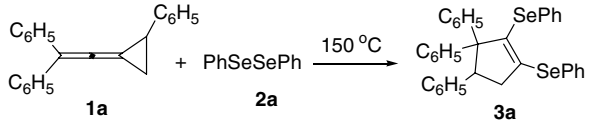
Abstract—Arylvinylidenecyclopropanes undergo a novel reaction upon heating at 150 °C with diaryl diselenide to give the corresponding 1,2-diarylselenocyclopentene derivatives in good to high yields within 1.5 h. The further transformation of 1,2-diarylselenocyclopentene derivatives has been disclosed.

Thermal and photochemical skeletal conversions of vinylidenecyclopropanes **1** have attracted much attention from mechanistic, theoretical, spectroscopic, and synthetic viewpoints in past decades.[1,2] Vinylidenecyclopropanes **1** also undergo a variety of unique addition reactions with electrophiles to give novel products sometimes along with the formation of cyclopropane ring-opened products.[3]

Previously, Ogawa and co-workers reported that the addition of diphenyl diselenide (PhSeSePh) to a number of alkynes produced *vic*-bis(phenylselenyl)alkenes at 150–180 °C for 10 h via radical-type scission.[4] Enlightened by their finding, we have reported the reactions of methylenecyclopropanes (MCPs) with diphenyl diselenide to give the corresponding ring-opened products in good yields at 150 °C.[5] In this letter, we attempted to examine the reactions of arylvinylidenecyclopropanes **1** with diaryl diselenide at high temperature under similar conditions. We first carried out the reaction of phenylvinylidenecyclopropane **1a** with diphenyl diselenide **2a** without an organic solvent at 150 °C, and found that the corresponding 1,2-diarylselenocyclopentene derivative **3a** (a five-membered ring product) was formed in good yield. The results are summarized in Table 1. The yield of **3a** can be improved using excess amounts of **2a** (Table 1, entries 1–3). In addition, when this reaction was directly carried out at 150 °C, the corresponding cyclized product **3a** was obtained in higher yield than the fact that the reaction temperature was gradually heated to 150 °C (Table 1, entries 2 and 3). This reaction is fairly effective and can complete within 1.5 h at 150 °C. Its structure was determined by ^{1}H and ^{13}C NMR spectroscopic data, and microanalysis

Table 1. The ring-opening reaction of phenylvinylidenecyclopropane **1a** with diphenyl diselenide **2a** at 150 °C



Entry	Molar ratio of **1** and **2a**	Time/(h)	Yield/(%)[b] **3a**
1[a]	1:1	1.5	79
2[a]	1:1.2	1.5	88
3[c]	1:1.2	1.5	97

[a] The reaction mixture was gradually heated to 150 °C and kept at this temperature for the time listed in this table.
[b] Isolated yields.
[c] The reaction mixture was directly put in the oil bath at 150 °C.

Keywords: Arylvinylidenecyclopropanes; Diaryl diselenides; Cyclopentene derivatives; Heating.
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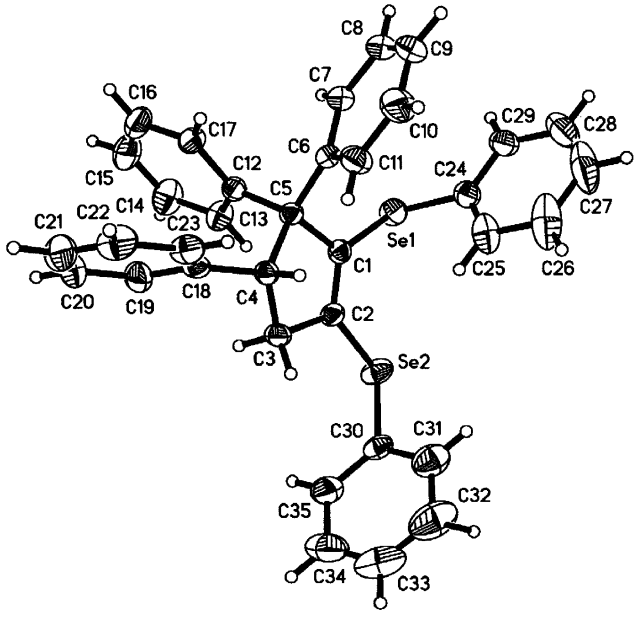


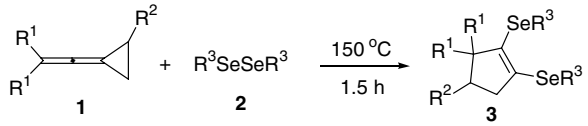
Figure 1. The ORTEP drawing of **3a**.

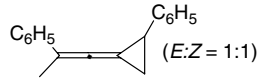
(see supporting information). Its crystal structure was further determined by X-ray diffraction (Fig. 1).[6]

A wide range of electronically and structurally diverse arylvinylidenecyclopropanes **1** and diaryl diselenide **2** can be employed in this reaction under these optimized conditions. The results are summarized in Table 2. As can be seen from Table 2, with respect to the electron-rich, electron-neutral, and electron-poor arylvinylidenecyclopropanes **1** (R^1 and R^2), they reacted with diaryl diselenide **2** smoothly to provide the corresponding 1,2-diarylselenocyclopentene derivatives **3** in good yields within 1.5 h in all of the cases (Table 2, entries 1–9). For unsymmetrical vinylidenecyclopropane **1i**, the corresponding cyclized product **3k** was obtained as *syn*/*anti* mixtures in 80% yield (Table 2, entry 10). Their spectroscopic and analytic data are shown in supporting information.

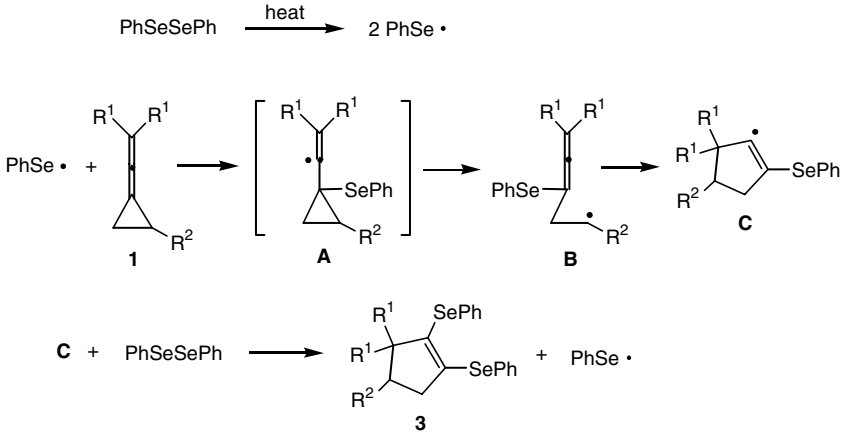
On the basis of previous investigations on the thermolysis of diphenyl diselenide,[7] a plausible mechanism for the reaction of arylvinylidenecyclopropanes **1** with diphenyl diselenide is outlined in Scheme 1. The phenylse-

Table 2. The ring-opening reaction of arylvinylidenecyclopropane **1** with diaryl diselenide **2** at 150 °C

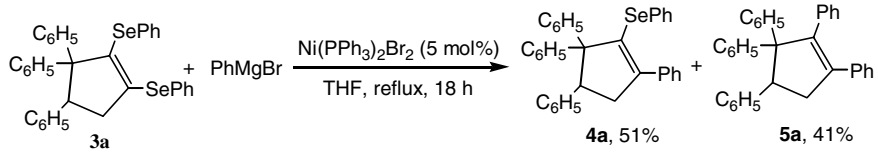


Entry[a]	**1** (R^1/R^2)	**2** (R^3)	Yield/(%)[b] **3**
1	**1b** (*p*-MeC_6H_4/C_6H_5)	**2a**	**3b**, 78
2	**1c** (*p*-$MeOC_6H_4$/C_6H_5)	**2a**	**3c**, 72
3	**1d** (*p*-FC_6H_4/C_6H_5)	**2a**	**3d**, 86
4	**1e** (*p*-ClC_6H_4/C_6H_5)	**2a**	**3e**, 61
5	**1f** (C_6H_5/*p*-ClC_6H_4)	**2a**	**3f**, 89
6	**1g** (C_6H_5/*p*-MeC_6H_4)	**2a**	**3g**, 82
7	**1h** (C_6H_5/*p*-$MeOC_6H_4$)	**2a**	**3h**, 62
8	**1a**	**2b** (*p*-MeC_6H_4)	**3i**, 79
9	**1a**	**2c** (*p*-$MeOC_6H_4$)	**3j**, 75
10	**1i**  (*E*:*Z* = 1:1)	**2a**	**3k**, 80 (10:3)[c]

[a] All the reactions were carried out in an oil bath 150 °C.
[b] Isolated yields.
[c] Ratio of *anti*/*syn*.



Scheme 1. The plausible reaction mechanism of arylvinylidenecyclopropanes **1** with diphenyl diselenide at 150 °C.



Scheme 2. The coupling reaction of **3a** with PhMgBr catalyzed by $Ni(PPh_3)_2Br_2$.

leno radical, produced by thermal cleavage of diphenyl diselenide, adds to the double bond of arylvinylidenecyclopropanes **1** to form the radical intermediate **A**, which immediately undergoes a homoallylic rearrangement to give another radical **B**.[5,8] The intramolecular cyclization of **B** produces the radical intermediate **C**. **C** reacts with another molecule of diphenyl diselenide via homolytic substitution (S_H) to produce the corresponding 1,2-diarylselenocyclopentene derivative **3** and regenerate a phenylseleno radical (Scheme 1).

The further transformation of **3a** is shown in Scheme 2. The coupling reaction of **3a** with excess amounts of phenylmagnesium bromide in the presence of $Ni(PPh_3)_2Br_2$ catalyst[9] produced the coupled products **4a** and **5a** in good total yields in THF under reflux (Scheme 2). The detailed results will be reported in due course.

In this letter, we disclosed a novel reaction of arylvinylidenecyclopropanes upon heating at 150 °C with diaryl diselenide to give the corresponding 1,2-diarylselenocyclopentene derivatives in good to high yields. These reactions complete within 1.5 h. The further possible transformation of **3** has been examined. Efforts are underway to elucidate the mechanistic details and to extend the scope of this novel reaction.

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Supplementary data

Supplementary data associated with this article can be found, in the online version at doi:10.1016/j.tetlet.2005.05.029.

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