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Reactions of Vinylidenecyclopropanes with Diphenyl Diselenide in the Presence of AIBN and Thermally-Induced Further Transformations

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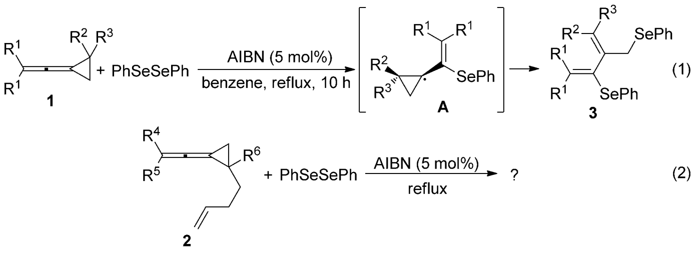
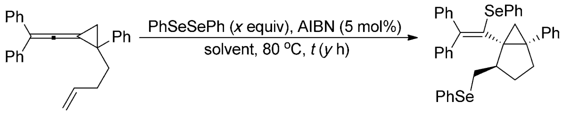
Vinylidenecyclopropanes (VDCPs) **1** bearing an allene moiety connected with a highly strained cyclopropane have been fascinating building blocks in organic synthesis and have attracted much attention from organic chemists.[1] In recent years, we and others have disclosed many useful transformations of VDCPs in the presence of Lewis or Brønsted acids as well as transition-metal catalysts, subsequently enriching the chemistry of VDCPs.[2–4] However, the chemistry of VDCPs having newly introduced functional groups such as alkene[4h] and hydroxyl group[4g] has been less developed thus far. Herein, we wish to report a new chemical transformation of VDCPs **2** (having an additional alkenyl group) with diphenyl diselenide in the presence of AIBN and further transformations of these products. In our previous work, we have reported that VDCPs **1** could react with diphenyl diselenide in the presence of AIBN to produce conjugate diene derivatives **3** in good yields through a radical intermediate **A** along with a further transformation (Scheme 1, reaction (1)).[5] Therefore, we envisaged that if we used VDCPs **2** as substrates to react with diphenyl diselenide in the presence of AIBN under the standard conditions, an interesting intermolecular reaction might be able to take place (Scheme 1, reaction (2)).



Scheme 1. Reactions of VDCPs with diphenyl diselenide in the presence of AIBN.

The initial examination was carried out using VDCP **2a** as the substrate to react with PhSeSePh (1.2 equiv) in the presence of AIBN (5 mol %) in benzene at 80 °C and we found that an interesting cyclized product **4a** was formed in 82 % yield within 3 h (Table 1, entry 1). Next, we attempted to optimize the reaction conditions and the results of these experiments are summarized in Table 1. As can be seen in Table 1, using toluene, 1,4-dioxane or acetonitrile (CH_3CN) as the solvent, **4a** could be also obtained in good yields (Table 1, entries 2–4). CH_3CN was the solvent of choice, affording the corresponding product **4a** in 90 % yield within 1 h (Table 1, entry 5). Increasing the employed amount of PhSeSePh did not improve the yield of **4a** (Table 1, entries 6 and 7). Dibenzoyl peroxide (BPO) was also found to be a useful radical initiator in this reaction (Table 1, entry 8), however, VDCP **2a** did not react with PhSSPh under identical conditions.

Table 1. Conditions screening for the reaction of VDCP **2a** with PhSeSePh in the presence of AIBN.



Entry[a]	Solvent	*x* [equiv]	*y* [h]	Yield [%][b]
1	benzene	1.2	3	82
2	toluene	1.2	3	84
3	1,4-dioxane	1.2	3	80
4	CH_3CN	1.2	3	84
5	CH_3CN	1.2	1	90
6	CH_3CN	1.5	1	86
7	CH_3CN	1.8	1	90
8[c]	CH_3CN	1.2	1	90

[a] The reactions were carried out using VDCPs **2a** (0.2 mmol), PhSeSePh (*x* equiv) and AIBN (5 mol %) in solvent at 80 °C with *x* equiv and *y* hours under argon. [b] Isolated product yields. [c] The reaction initiator was BPO (dibenzoyl peroxide).

Under the optimized reaction conditions, the substrate scope and limitations of the reaction were explored and the results are summarized in Table 2. As shown in Table 2, as for VDCPs **2b**–**2l**, in which R^1, R^2, and R are aromatic groups, could react smoothly with PhSeSePh to give the corresponding products **4b**–**4l** in 67–94 % yields whether they

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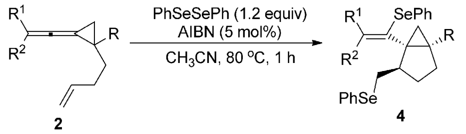
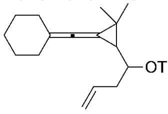
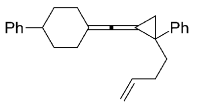
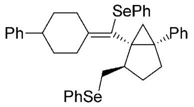
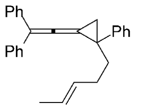
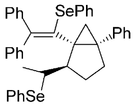
Supporting information for this article (including spectroscopic charts of the compounds shown in Tables 1–3, X-ray crystal data of **4i**, **5l**, and **6a** as well as the detailed descriptions of experimental procedures) is available on the WWW under http://dx.doi.org/10.1002/chem.201103461.

Table 2. Substrate scope of VDCPs **2** with PhSeSePh in the presence of AIBN.



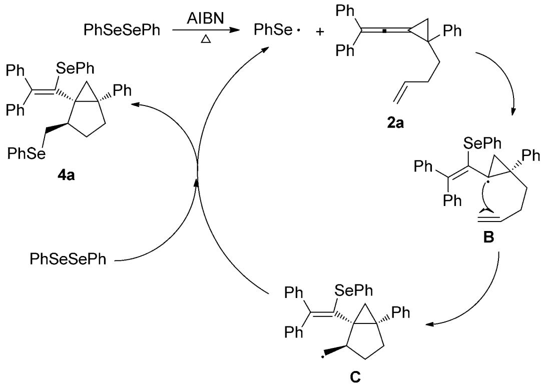
Entry[a]	$R^1/R^2/R$	2	4	Yield [%][b]
1	$C_6H_5/C_6H_5/p\text{-}FC_6H_4$	**2b**	**4b**	87
2	$C_6H_5/C_6H_5/p\text{-}ClC_6H_4$	**2c**	**4c**	85
3	$C_6H_5/C_6H_5/p\text{-}BrC_6H_4$	**2d**	**4d**	89
4	$C_6H_5/C_6H_5/m\text{-}BrC_6H_4$	**2e**	**4e**	89
5	$C_6H_5/C_6H_5/p\text{-}CH_3C_6H_4$	**2f**	**4f**	94
6	$C_6H_5/C_6H_5/p\text{-}CH_3OC_6H_4$	**2g**	**4g**	67
7	$p\text{-}ClC_6H_4/C_6H_5/C_6H_5$	**2h**	**4h**	90[c]
8	$p\text{-}ClC_6H_4/p\text{-}ClC_6H_4/C_6H_5$	**2i**	**4i**	91
9	$p\text{-}CH_3C_6H_4/p\text{-}CH_3C_6H_4/C_6H_5$	**2j**	**4j**	86
10	$p\text{-}CH_3OC_6H_4/p\text{-}CH_3OC_6H_4/C_6H_5$	**2k**	**4k**	85
11	$p\text{-}BrC_6H_4/p\text{-}BrC_6H_4/p\text{-}BrC_6H_4$	**2l**	**4l**	81
12	$C_6H_5/C_6H_5/CH_3$	**2m**	**4m**	36[d]
13		**2n**		–
14		**2o**	**4o** 	91
15		**2p**	**4p** 	91

[a] The reactions were carried out using VDCPs **2** (0.2 mmol), PhSeSePh (1.2 equiv) and AIBN (5 mol%) in CH_3CN at 80 °C within 1 h under argon. [b] Isolated product yields. [c] *E*- or *Z*-isomeric mixture (ratio = 1.2:1). [d] The yield was determined by ^1H NMR spectroscopic data (1,3,5-trimethoxybenzene as internal standard).

have electron-withdrawing or electron-donating substituents on their aromatic rings (Table 2, entries 1–11). As for VDCPs **2h**, in which R^1 and R^2 were different aromatic groups, the corresponding product **4h** was obtained as an *E*/*Z* isomeric mixture with a ratio of 1.2:1 (Table 2, entry 7). In the case of VDCP **2m**, in which R^1 and R^2 were aromatic groups and R is a methyl group, the corresponding product **4m** was formed in 36% yield (Table 2, entry 12). Using alkyl-substituted VDCP **2n** as substrate, no reaction occurred (Table 2, entry 13); however, using alkyl-substituted VDCP **2o** as the substrate, the desired product **4o** could be also obtained in 91% yield as a mixture of diastereoisomers (Table 2, entry 14). Furthermore, VDCP **2p** tethered with a methyl group with an olefin could also react with PhSeSePh smoothly to give the corresponding product **4p** in 91% yield (Table 2, entry 15), suggesting a wide substrate scope. The structure of **4i** has been unambiguously determined by X-ray diffraction (see the Supporting Information). Attempts to synthesize other alkyl-substituted substrates failed to give the desired products (see the Supporting Information for more details).

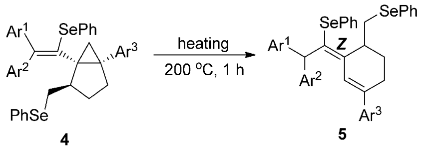
On the basis of the previous literature,[5,6] a plausible mechanism for the formation of **4** has been presented in Scheme 2 by using **2a** as the reaction model. First, the newly formed phenyl selenium radical in the presence of AIBN adds to the allene moiety of VDCP **1a** to give the corresponding radical intermediate **B**, which undergoes an intramolecular radical addition to give the radical intermediate **C**. Then, intermediate **C** reacts with another molecule of PhSeSePh to give the corresponding bicyclo[3.1.0]hexane derivative **4a** along with the regeneration of another phenyl selenium radical to accomplish the radical reaction cycle (Scheme 2). Moreover, the reaction of VDCP **2p** tethered with a 4-pentenyl group with PhSe radical proceeded smoothly to give the corresponding product **4p** in high yield under the standard conditions (Table 2, entry 15), suggesting that the benzeneselenenyl radical would not add to the tethered butenyl chain since this addition could retard the reaction rate significantly.

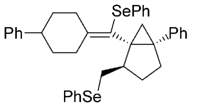
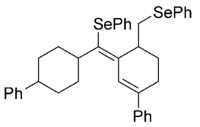
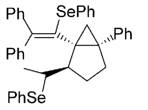
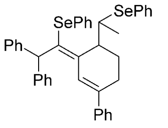
Since products **4** are bicyclo[3.1.0]hexane derivatives and contain an vinylic cyclopropane moiety, they can further undergo radical ring-opening/closing reactions at high temperature.[7] Therefore, by using **4a** as a reactant, we attempted to explore the further transformation of **4a**. It was found that upon heating at 200 °C without any solvent, a new cyclohexene derivative **5a** could be obtained within 1 h in 97% yield stereoselectively in the *Z* configuration (Table 3, entry 1) and no reaction occurred upon heating at < 190 °C. The substrate scope has also been



Scheme 2. A plausible reaction mechanism on the formation of **4a**.

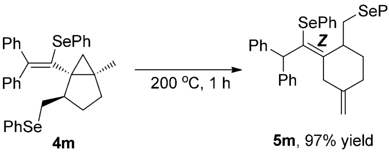
Table 3. Substrate scope of thermal-induced rearrangement of **4** upon heating at 200 °C.



Entry[a]	Ar^1/Ar^2/Ar^3	4	5	Yield [%][b]
1	C_6H_5/C_6H_5/C_6H_5	**4a**	**5a**	97
2	C_6H_5/C_6H_5/*p*-FC_6H_4	**4b**	**5b**	97
3	C_6H_5/C_6H_5/*p*-ClC_6H_4	**4c**	**5c**	97
4	C_6H_5/C_6H_5/*m*-BrC_6H_4	**4e**	**5e**	89
5	C_6H_5/C_6H_5/*p*-$CH_3C_6H_4$	**4f**	**5f**	93
6	C_6H_5/C_6H_5/*p*-$CH_3OC_6H_4$	**4g**	**5g**	85
7	*p*-ClC_6H_4/C_6H_5/C_6H_5	**4h**	**5h**[c]	92
8	*p*-ClC_6H_4/*p*-ClC_6H_4/C_6H_5	**4i**	**5i**	92
9	*p*-$CH_3C_6H_4$/*p*-$CH_3C_6H_4$/C_6H_5	**4j**	**5j**	87
10	*p*-BrC_6H_4/*p*-BrC_6H_4/*p*-BrC_6H_4	**4l**	**5l**	97
11		**4o**	**5o** 	97
12		**4p**	**5p** 	97

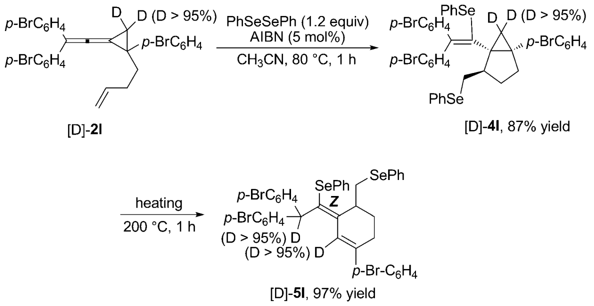
[a] Reactions were carried out without any solvents at 200 °C within 1 h under argon. [b] Isolated product yields. [c] Containing a pair of diastereomeric isomers, ratio: 1:1

investigated and the results are summarized in Table 3. The thermal-induced rearrangement of compounds **4a**–**4c** and **4e**–**4l** proceeded smoothly to give the corresponding products **5a**–**5c** and **5e**–**5l** in 85–97 % yields, suggesting that the electronic property of R^1, R^2, and R^3 aromatic groups have no influence on the reaction outcome (Table 3, entries 1–10). Using alkyl-substituted **4o** as the substrate, the corresponding rearrangement product **5o** could be also obtained in 97 % yield (Table 2, entry 11) and substrate **4p** could be also transformed to the desired product **5p** in 97 % yield (Table 2, entry 12). As for product **4m**, in which R is a methyl group, a double bond migrated product **5m** was obtained in 97 % yield under identical conditions (Scheme 3). The structure of **5l** has been unambiguously determined by X-ray diffraction to be in the *Z* configuration (see the Supporting Information).



Scheme 3. Thermal-induced rearrangement of **4m** upon heating at 200 °C.

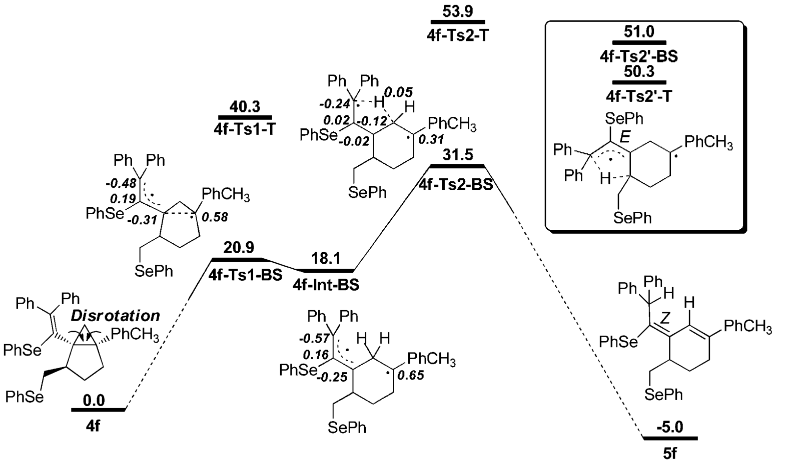
It seems to us that the corresponding product **5** was produced through a new radical 1,4-H migration.[6b,8] To gain more mechanistic insight into the reaction, we performed an isotope labeling experiment to examine the reaction outcome by using dideuterated **2l** (Scheme 4, [D]-**2l**) as the reactant and the reactions were carried out under the standard conditions (Scheme 4; for the details, see the Supporting Information). It was found that product [D]-**4l** could be obtained in 87 % yield along with D content > 95 %, which could also undergo thermal-induced rearrangement to give the corresponding product [D]-**5l** in 97 % yield along a complete 1,4-D shift. Moreover, as for the formation of **5l** and [D]-**5l** by employing **4l** and [D]-**4l** as reactants, a kinetic isotope effect $k_H/k_D \approx 1.5$ was observed at 200 °C under the standard conditions (see the Supporting Information), suggesting that the C−H bond cleavage is the rate-determining step and the reaction proceeded through a radical pathway.[9]



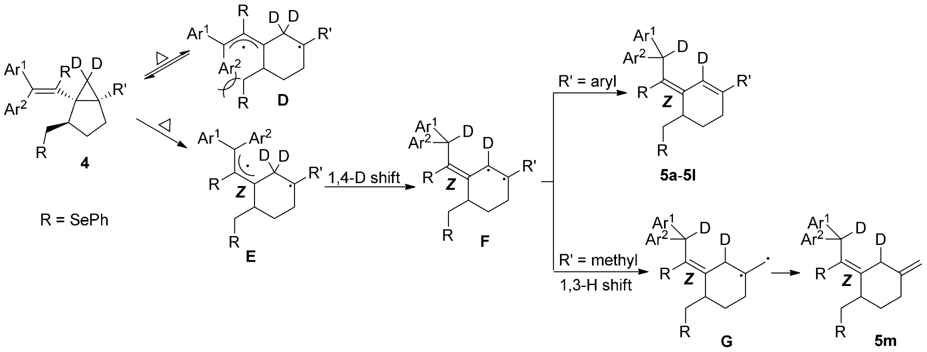
Scheme 4. Isotope labeling experiments.

Density functional theory (DFT)[10] studies have also been performed at UB3LYP[11]/6-31G* level with Gaussian 09 program to investigate the reaction pathway in the formation of **5** from **4**.[12] To obtain more accurate energies, single point calculations have been performed with the 6-311+G** basis set. For each structure, harmonic vibration frequency calculations have been carried out and thermal corrections have been undertaken. All structures have been shown as the transition states (with one imaginary frequency) or the stationary points (with no imaginary frequency).

The substrate **4f** (Ar^1 = Ar^2 = Ph, Ar^3 = *p*-$CH_3C_6H_4$) was used in the calculation and the proposed reaction pathways are shown in Scheme 5. In this reaction, the transition states and intermediates are all characterized as biradicals. Their



Scheme 5. The calculated reaction pathway in the formation of **5f** has been indicated. The selected Mulliken spin densities are shown as italic and the relative free energies ΔG (298 K) are in kcal mol^{-1} calculated at the UB3LYP/6-311+G**//UB3LYP/6-31G* level.



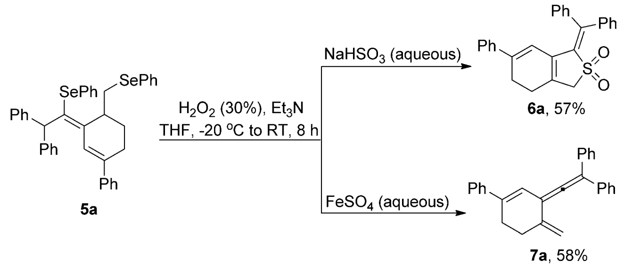
Scheme 6. A plausible reaction mechanism for the formation of **5**.

primary structures can be considered as derivatives of trimethylene biradicals, which has been well studied in the isomerization of cyclopropane to propene.[13] The triplet states and broken-symmetry (BS) singlet states have been considered in the calculation. The results showed that the energies of the triplet transition states are much higher than those of singlet ones (**4f-Ts1-T**, 40.3 kcal mol^{-1}, **4f-Ts2-T**, 53.9 kcal mol^{-1}). Consequently the triplet state pathway can be excluded. This result is also consistent with the previous experimental observations that trimethylene is a singlet biradical.[13a,b]

In the first step, the cyclopropane unit in **4f** undergoes a homolytic C−C bond cleavage through the singlet disrotation ring-opening transition state **4f-Ts1-BS** (20.9 kcal mol^{-1}), leading to the slightly more stable singlet biradical intermediate **4f-Int-BS** (18.1 kcal mol^{-1}) (see the Supporting Information; Figure SI-6). The recombination of **4f-Int-BS** is very fast because it just needs to overcome an energy barrier of 2.8 kcal mol^{-1}. This result is consistent with the high level calculation of cyclopropane ring-opening process.[13c,d] Due to the delocalization of the radicals to the substituents, the opening barrier is much lower for **4f** compared with that of cyclopropane (about 65 kcal mol^{-1}).[13d] The subsequent 1,4-hydrogen transfer through **4f-Ts2-BS** (31.5 kcal mol^{-1}) yields the corresponding product **5f** in the *Z* configuration (see the Supporting Information; Figure SI-6). The overall barrier is 31.5 kcal mol^{-1}, which is reasonable for a reaction occurring at 200 °C. The second step is the rate-determining step, which is also consistent with the deuterium labeling experiment. As shown in the rectangle in Scheme 5, the transition states of the diphenylmethylene group abstracts the other neighboring hydrogen atom (**4f-Ts2′-BS**, 51.0 kcal mol^{-1}; **4f-Ts2′-T**, 50.3 kcal mol^{-1}) can lead to another biradical intermediate. However, this reaction pathway can be excluded due to the high energy barrier. Therefore, the product (in which the double bond has an *E* configuration) cannot be formed.

On the basis of the above experiments and DFT calculations, the mechanism for the formation of **5** has been outlined in Scheme 6. Initially, bicyclo[3.1.0]hexane derivative **4** undergoes a homolytic cleavages of C−C bond upon heating at 200 °C to give the corresponding biradical intermediate **D** or intermediate **E** (*Z* configuration). The biradical intermediate **D** is unstable because it suffers from the steric repulsion between aromatic group and the CH_2SePh group. The biradical intermediate **E** can abstract the hydrogen atom to give the corresponding biradical intermediate **F** in the *Z* configuration. The recombination of biradical intermediate **F** gives the cyclohexene derivative **5** when R′ is an aromatic group (Scheme 6). On the other hand, when R′ is a methyl group, the biradical intermediate **F** undergoes a radical 1,3-hydrogen shift and then a recombination to give the corresponding product **5m** (Scheme 6).

Aryl selenides can be easily oxidized to the corresponding selenoxides, which can undergo a variety of interesting rearrangements through the elimination.[14,15] Therefore, further transformation of **5a** was performed in the presence of H_2O_2 (30 % aqueous solution) at low temperature. We found that the cyclization product **6a** was obtained in 57 % yield when the reaction was quenched by saturated $NaHSO_3$ aqueous solution, but an allenic derivative **7a**[16] was formed in 58 % yield when the reaction was quenched by saturated $FeSO_4$ aqueous solution (Scheme 7). The structure of **6a** was unambiguously determined by X-ray diffraction and it



Scheme 7. Further transformation of **5a** in the presence of H_2O_2.

was formed through the reaction of **7a** with the in situ generated SO_2 during the quenching process (see the Supporting Information).

In conclusion, we have developed a novel tandem reaction of VDCPs **1** with PhSeSePh to give the corresponding bicyclo[3.1.0]hexane derivatives **4** in good yields in the presence of AIBN, which could undergo a thermal-induced radical 1,4-hydrogen shift through a ring-opening pathway of allylic cyclopropane to give the corresponding cyclohexene derivatives **5** stereoselectively in the *Z* configuration and in good yields at 200 °C. Plausible reaction mechanisms have been also proposed on the basis of deuterium labeling experiments and DFT calculations. In addition, the cyclohexene derivative **5a** can be transformed into cyclic sulphone **6a** and allene **7a** in moderate yields in the presence of H_2O_2. Further investigations on the mechanistic details of the reaction as well as the further exploration of other useful chemical transformations of vinylidenecyclopropanes are in progress.

Acknowledgements

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Keywords: 1,4-hydrogen shift · diphenyl diselenide · oxidation · radical reactions · ring-opening · vinylidenecyclopropanes

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