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Reactions of Vinylidenecyclopropanes with Diphenyl Diselenide in the Presence of AIBN and Further Transformation To Produce New Naphthalene Derivatives

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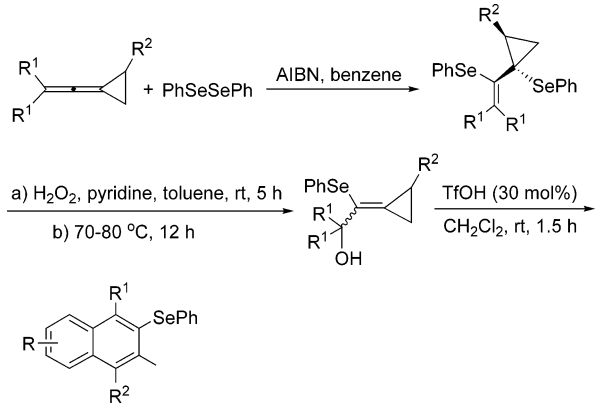

The reactions of vinylidenecyclopropanes **1** with diphenyl diselenide **2** in the presence of AIBN produced the corresponding products **4** or **5** in moderate to good yields under mild conditions. The transformation of **4** to the corresponding methylenecyclopropanes **6** was achieved by treatment with hydrogen peroxide (H_2O_2) in toluene, and these were further transformed to the corresponding naphthalene derivatives **7** by treatment with 30 mol % of TfOH in dichloromethane.

Introduction

Vinylidenecyclopropanes **1** are highly strained and reactive allenes which undergo a number of facile cycloadditions reactions [1] and other transformations[2] of synthetic utility. Furthermore, selenium-containing organic molecules are also very useful compounds in synthetic organic chemistry.[3] The arylselenyl (ArSe−) and alkylselenyl (RSe−) functional groups have tremendous synthetic utility by virtue of their versatile and well-behaved transformations.[4] We have recently reported the reaction of vinylidenecyclopropanes **1** with diaryl diselenide **2** catalyzed by iodosobenzene diacetate **3** to give the corresponding addition products **4** in moderate to good yields under mild conditions via a cationic process (Scheme 1).[5]

During our ongoing investigation of this interesting addition reaction, we found that vinylidenecyclopropanes **1** can also react

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(4) Yao, Q.-W.; Kinney, E. P.; Zheng, C. *Org. Lett.* **2004**, *6*, 2997.

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SCHEME 1. Reactions of Vinylidenecyclopropanes 1 with Diaryl Diselenide 2 in the Presence of Iodosobenzene Diacetate 3

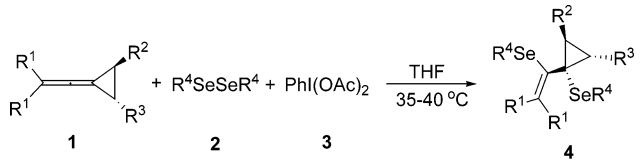
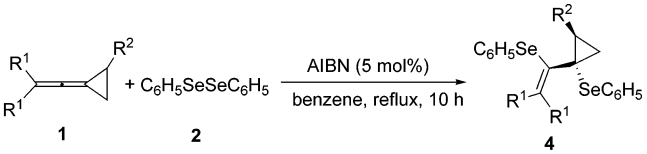
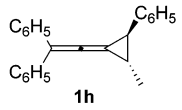
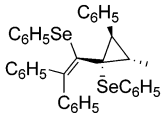


TABLE 1. Reaction of Vinylidenecyclopropanes 1 with Diphenyl Diselenide 2 in the Presence of AIBN (5 mol %)



entry[a]	**1** (R^1/R^2)	yield/(%)[b]
1	**1a** (C_6H_5/C_6H_5)	**4a**, 92
2	**1a** (C_6H_5/C_6H_5)	**4a**, 53[c]
3	**1b** (p-MeC_6H_4/C_6H_5)	**4b**, 88
4	**1c** (p-FC_6H_4/C_6H_5)	**4c**, 79
5	**1d** (p-ClC_6H_4/C_6H_5)	**4d**, 58
6	**1e** (C_6H_5/p-ClC_6H_4)	**4e**, 69
7	**1f** (C_6H_5/p-MeC_6H_4)	**4f**, 83
8	**1g** (C_6H_5/p-$MeOC_6H_4$)	**4g**, 66
9		 **4h**, 48

[a] All reactions were carried out using **1** (0.2 mmol), **2** (0.24 mmol), and AIBN (0.01 mmol) in benzene (1.0 mL) under reflux. [b] Isolated yields.[c] 5 mol % of BPO was used.

with diphenyl diselenide in the presence of AIBN to give the same products **4** via a radical process in good yields. Additionally, the conversion of **4** to the corresponding methylenecyclopropanes (MCPs) **6** has also been comprehensively examined. Moreover, these novel MCPs can be easily converted to the corresponding naphthalene derivatives **7** in good yields in the presence of TfOH. Herein, the full details of these reactions are described.

Results and Discussion

Initial examination showed that when the radical initiator 2,2′-azobis(2-methylpropionitrile) (AIBN) or benzoyl peroxide (BPO) was added to the solution, the reaction of vinylidenecyclopropane **1a** with diphenyl diselenide proceeded smoothly to give the corresponding addition product **4a** in 92% and 53% yields, respectively, in refluxing benzene (Table 1, entries 1 and 2). The results are summarized in Table 1. For a variety of symmetrical vinylidenecyclopropanes **1b**−**h**, the corresponding addition products **4b**−**h** were obtained in moderate to good yields (Table 1, entries 3−9). The structures of the products were determined by NMR spectroscopic data, microanalysis, and HRMS (Supporting Information). The stereochemistry of product **4a** has been determined by X-ray diffraction.[5]

A plausible mechanism for the formation of products **4** is shown in Scheme 2. The phenylseleno radical **A**, which is

SCHEME 2. Plausible Mechanism for the Formation of 4a−h

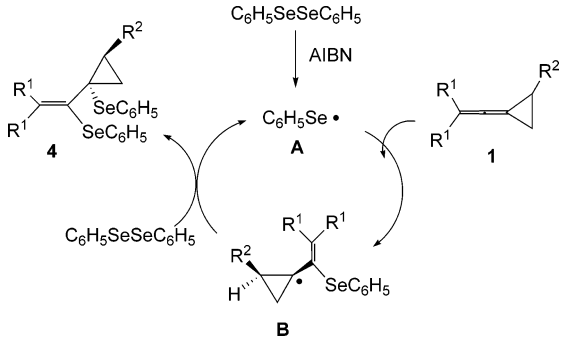
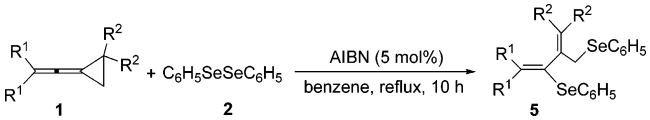


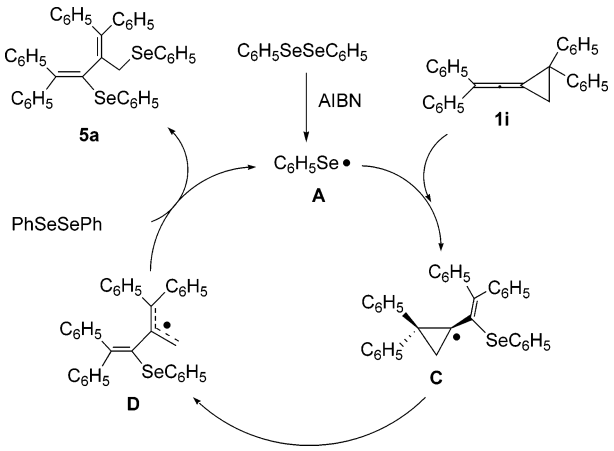
TABLE 2. Reactions of Vinylidenecyclopropanes 1i−k with Diphenyl Diselenide 2 in the Presence of 5 mol % of AIBN



entry[a]	**1** (R^1/R^2)	yield[b] (%)
1	**1i** (C_6H_5/C_6H_5)	**5a**, 66
2	**1j** (C_6H_5/p-ClC_6H_4)	**5b**, 43
3	**1k** (C_6H_5/p-$CH_3C_6H_4$)	**5c**, 57

[a] All reactions were carried out using **1** (0.2 mmol), **2** (0.24 mmol), and AIBN (0.01 mmol) in benzene (1.0 mL) under reflux. [b] Isolated yields.

SCHEME 3. Plausible Mechanism for the Formation of 5a

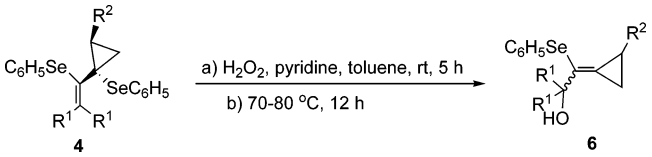


generated by cleavage of diphenyl diselenide with AIBN, adds to the double bond of vinylidenecyclopropanes **1** from the opposite side of the R^2 group, presumably due to the steric repulsion between the R^2 and PhSe groups, to form the corresponding radical intermediate **B**.[6] Intermediate **B** reacts with another diphenyl diselenide molecule in the same manner, opposite from the R^2 group, to afford product **4** with regeneration of the phenylseleno radical **A**.

Furthermore, we found that diaryl-substituted vinylidenecyclopropanes **1i**−**k** reacted with diphenyl diselenide in the presence of AIBN to give the corresponding ring-opened products **5a**−**c** in moderate yields (Table 2, entries 1−3). The proposed mechanism for the formation of **5a**−**c** is shown in Scheme 3. The cyclopropane radical intermediate **C** undergoes ring-opening to give allylic radical intermediate **D** since substitution by the two phenyl rings in the 3-position of the

(6) Pasto, D. J.; Miels, F. M. *J. Org. Chem.* **1976**, *41*, 2068.

TABLE 3. Further Transformation of 4 by H_2O_2 (5.0 equiv) with Pyridine (2.0 equiv) in Toluene



entry	**4** (R^1/R^2)	yield[b] (%)	E/Z[c,d]
1	**4a** (C_6H_5/C_6H_5)	**6a**, 55	7:1
2	**4b** (p-MeC_6H_4/C_6H_5)	**6b**, 40	50:1
3	**4c** (p-FC_6H_4/C_6H_5)	**6c**, 54	>200:1
4	**4d** (p-ClC_6H_4/C_6H_5)	**6d**, 63	8:1
5	**4e** (C_6H_5/p-ClC_6H_5)	**6e**, 72	7:1
6	**4f** (C_6H_5/p-MeC_6H_4)	**6f**, 68	4:1
7	**4g** (C_6H_5/p-$MeOC_6H_4$)	**6g**, 42	3:1

[a] All reactions were carried out with **4** (0.1 mmol), H_2O_2 (5 equiv), and pyridine (2.0 equiv) in toluene (1.0 mL). [b] Isolated yields. [c] The stereochemistry of **6c** was determined by NOESY, and the other compounds were tentatively assigned according to the general trend. [d] Determined by ^1H NMR spectroscopic data.

allylic radical intermediate **D** leads to a greater resonance stabilization than observed in simple allylic radicals.[7] Radical intermediate **D** reacts with another diphenyl diselenide to produce the corresponding ring-opened products **5a**−**c** with regeneration of the radical **A**. The two *gem*-aryl groups on the cyclopropane ring of **1** are essential for the ring-opening reaction to occur.

The further transformation of addition products **4** was examined by treatment of them with hydrogen peroxide (H_2O_2) in the presence of pyridine.[8] We found that a series of novel MCPs **6** were formed in moderate to good yields in toluene at room temperature for 5 h and then at 70−80 °C for 12 h as mixtures of *E*/*Z* isomers. The results are summarized in Table 3. Triethylamine, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), and piperidine could also used as the base in these reactions, but pyridine gave the best result. The product structures were determined by NMR spectroscopic data, microanalyses, HRMS, and X-ray diffraction. The X-ray crystal structure of *E*-**6f** is shown in Figure 1.[9] In addition, the *E*/*Z* ratios of **6** shown in Table 3 were determined by ^1H NMR spectroscopy, including NOESY data (Supporting Information).

The formation of methylenecyclopropanes **6** can be rationalized through a[2,3]-sigmatropic rearrangment on the basis of previous reports (Scheme 4).[10] Selenide **4**, which has two conformations (**4A** and **4B**), is oxidized by H_2O_2 to form the corresponding intermediates **4E**^{1} and **4E**^{2}, respectively. Because of the steric repulsion between the R^2 and PhSe groups in **4B**, **4A** should be the major conformer. Therefore, selenoxide **4E**^{1} is the major product, which leads to intermediate **4F**^{1} via a[2,3]-sigmatropic rearrangement. After treatment with aqueous saturated Na_2SO_3 solution in pyridine, product *E*-**6** was obtained as the major product (Scheme 4). For **4c**, having a fluorine atom

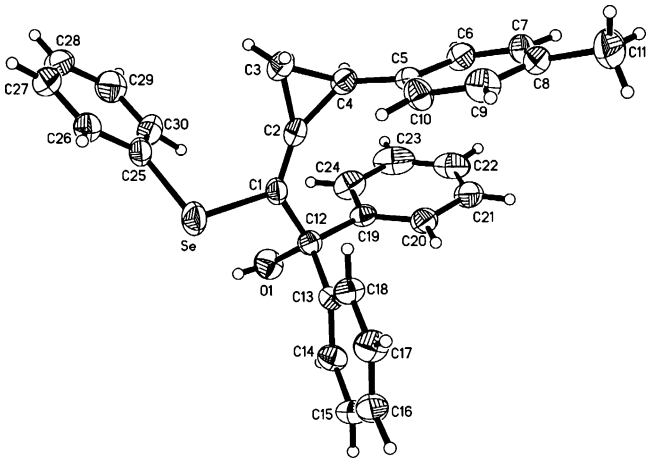
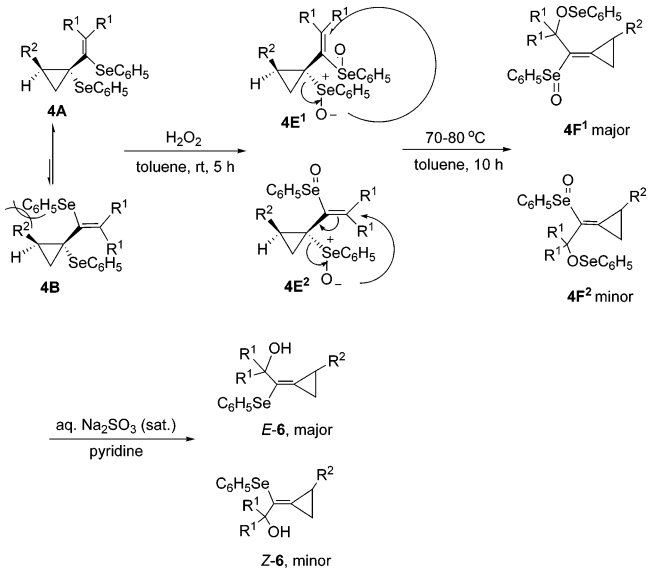


FIGURE 1. ORTEP drawing of *E*-**6f**.

SCHEME 4. Plausible Mechanism for the Transformation of 4

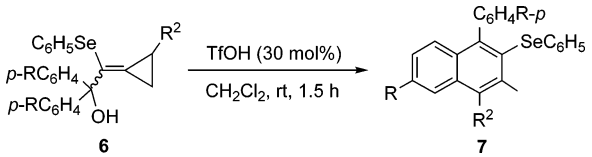


at the para position of the aryl ring, the corresponding MCP *E*-**6c** was formed in a >200:1 ratio, presumably due to the strongly electron-withdrawing nature of fluorine atom in addition to the steric effects (Table 3, entry 3).

Interestingly, during our investigations of the further transformation of the obtained products **6**, we found that a series of naphthalene derivatives **7** were formed in moderate to good yields by the treatment of **6** with trifluoromethanesulfonic acid (CF_3SO_3H/TfOH) (30 mol %) in dichloromethane at room temperature for 1.5 h (Table 4, entries 1−7). A plausible reaction mechanism is shown in Scheme 5. We believe that upon treatment of **6a** with TfOH, a cationic intermediate **F** is formed.[11] The allylic rearrangement of cationic intermediate **F** produces the corresponding cationic intermediate **G**, which undergoes ring-opening to generate the intermediate **H**.[12] The

(7) Walborsky, H. M.; Chen, J.-C. *J. Am. Chem. Soc.* **1970**, *92*, 7573.
(8) (a) Halazy, S.; Krief, A. *Tetrahedron Lett.* **1981**, *22*, 2135. (b) Liu, L.-P.; Shi, M. *Chem. Commun.* **2004**, 2878.
(9) The crystal data of *E*-**6f** has been deposited at the CCDC, no. 270772: empirical formula, $C_{30}H_{26}OSe$; formula weight, 481.47; crystal color, habit, colorless, prismatic; crystal system, monoclinic; lattice type, primitive; lattice parameters, a = 10.0830(10) Å, b = 9.6407(10) Å, c = 25.028(3) Å, $\alpha = 90°$, $\beta = 101.187(2)°$, $\gamma = 90°$, V = 2386.6(4) Å^3; space group, $P2(1)/n$; Z = 4; D_{calc} = 1.340 g/cm^3; F_{000} = 992; diffractometer: Rigaku AFC7R; residuals R, R_w, 0.0408, 0.0769.
(10) For a recent review, see: Reich, H. J. *Organoselenium Chemistry*; Liotta, D., Ed.; Wiley-Interscience: New York, 1987; pp 365−394.
(11) (a) Denmark, S. E.; Chen, C.-T. *Tetrahedron lett.* **1994**, *35*, 4327. (b) Freund, T.; Scherf, U.; Mullen. K. *Angew. Chem.* **1994**, *33*, 2424. (c) Chen, C.-T.; Chao, S.-D.; Yen, K.-C.; Chen, C.-H.; Chou, I.-C.; Hon, S.-W. *J. Am. Chem. Soc.* **1997**, *46*, 11341.
(12) (a) Applequist, D. E.; Nickel, G. W. *J. Org. Chem.* **1979**, *44*, 321. (b) Brown, H. C.; Rao, C. G.; Ravindranathan, M. *J. Am. Chem. Soc.* **1978**, *100*, 7946.

TABLE 4. Treatment of 6 with TfOH (30 mol %)

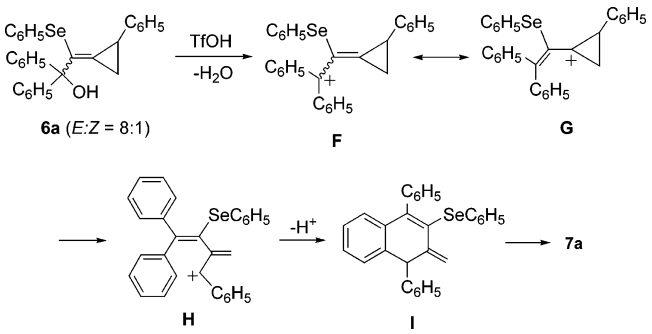


6 7

entry	**6** (R^1/R^2)	**6** (*E*/*Z*)	yield[b] (%)
1	**6a** (H/C_6H_5)	7:1	**7a**, 94
2	**6b** (Me/C_6H_5)	50:1	**7b**, 86
3	**6c** (F/C_6H_5)	>200:1	**7c**, 74
4	**6d** (Cl/C_6H_5)	8:1	**7d**, 69
5	**6e** (H/*p*-ClC_6H_4)	7:1	**7e**, 83
6	**6f** (H/*p*-MeC_6H_4)	4:1	**7f**, 88
7	**6g** (H/*p*-$MeOC_6H_4$)	3:1	**6g**, 42

[a] All reactions were carried out with **6** (0.1 mmol) and TfOH (30 mol %) in CH_2Cl_2 (1.0 mL). [b] Isolated yields.

SCHEME 5. Plausible Mechanism for the Transformation of 5a



intramolecular Friedel−Crafts reaction affords the intermediate **I** from which the corresponding naphthalene derivative **7a** is ultimately produced via an aromatization process (Scheme 3).

Conclusions

We have disclosed an interesting radical addition reaction of vinylidenecyclopropanes with diphenyl diselenide in the presence of AIBN to give the corresponding products **4a**−**h** or **5a**−**c** in moderate to good yields under mild reaction conditions. The further transformation of **4a**−**g** has been also examined in the presence of hydrogen peroxide (H_2O_2) in toluene. The corresponding MCPs **6a**−**g** were formed in moderate yields, and these can be easily converted to the corresponding naphthalene derivatives **7a**−**g** by treatment with TfOH. Efforts are underway to confirm the mechanistic details of these reactions and their scope and limitations.

Experimental Section

General Procedure for the Reaction of Vinylidenecyclopropanes 1 with Diphenyl Diselenide in the Presence of AIBN. Under an argon atmosphere, vinylidenecyclopropanes **1** (0.2 mmol), diphenyl diselenide (0.24 mmol), AIBN (0.01 mmol), and benzene (1.0 mL) were added to a Schlenk tube. The mixture was stirred under reflux for 10 h, and then the solvent was removed under reduced pressure and the residue was purified by flash column chromatography.

General Procedure for the Reaction of Products 4 with Hydrogen Peroxide (H_2O_2) and Pyridine in Toluene. Compound **4** (0.1 mmol), 30% H_2O_2 (0.05 mL), pyridine (0.2 mmol), and toluene (1.0 mL) were placed in a Schlenk tube. The mixture was stirred at room temperature for 5 h, and then it was further stirred at 70−80 °C for an additional 12 h. The mixture was diluted with 10 mL of saturated Na_2SO_3 solution and extracted with Et_2O (3 × 5.0 mL). The combined organic layers were dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure, and the residue was purified by flash column chromatography.

General Procedure for the Reaction of Compound 6 in the Presence of TfOH. Under an argon atmosphere, compound **6** (0.1 mmol), 30 mol % of TfOH (0.03 mmol), and CH_2Cl_2 (1.0 mL) were added into a Schlenk tube. The reaction mixture was stirred at room temperature for 1.5 h, and then the solvent was removed under reduced pressure and the residue was purified by flash column chromatography.

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Supporting Information Available: ^1H and ^{13}C NMR spectroscopic data and analytic data for compounds **4**−**7** and X-ray crystal data of *E*-**6f**. This material is available free of charge via the Internet at http://pubs.acs.org.

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