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Thermal Rearrangement of {[2-(Arylmethylene)cyclopropyl]methyl}(phenyl)sulfanes and Selanes

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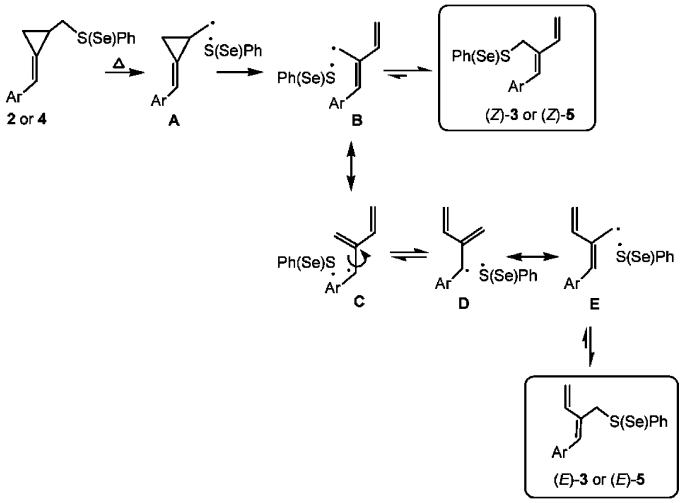

{[2-(Arylmethylene)cyclopropyl]methyl}(phenyl)sulfanes and {[2-(arylmethylene)cyclopropyl]methyl}-(phenyl)selanes, generated in situ from 2-(arylmethylene)cyclopropylcarbinols with sodium benzenethiolate and sodium benzeneselenolate, could undergo rearrangement upon heating to afford (2-arylmethylidenebut-3-enyl)(phenyl)sulfanes and (2-arylmethylidenebut-3-enyl)(phenyl)selanes, in good to excellent yields as mixtures of *E*- and *Z*-isomers, respectively. A radical rearrangement was proposed on the basis of control experiments for this process.

Introduction

Methylenecyclopropanes (MCPs) are highly strained but readily accessible and stable molecules that serve as useful building blocks in organic synthesis. MCPs undergo a variety of ring-opening reactions because the relief of ring strain provides a potent thermodynamic driving force.[1] In the past decade, transition-metal (such as Pd, Rh, Ru, and Pt)-catalyzed reactions of MCPs with various reactants have been studied systematically by chemists.[2] Recently, we and others found that Lewis acid was also powerful catalyst for MCPs to undergo ring-opening and cycloaddition reactions with heteroatom-containing molecules.[3] 2-(Arylmethylene)cyclopropylcarbinols **1**, methylenecyclopropanes bearing an additional hydroxymethyl group, could undergo different reactions from MCPs under mild conditions as demonstrated by our group.[4] Herein, we wish to report a radical rearrangement of {[2-(arylmethylene)cyclopropyl]-methyl}(phenyl)sulfanes **2** and {[2-(arylmethylene)cyclopropyl]-methyl}(phenyl)selanes **4**, derived from the reaction of mesylated **1** with sodium benzenethiolate and sodium benzeneselenolate, affording (2-arylmethylidenebut-3-enyl)(phenyl)sulfanes **3** and (2-arylmethylidenebut-3-enyl)(phenyl) selanes **5** in good to excellent yields, respectively.

Results and Discussion

At the beginning of our investigation, we attempted to prepare (*E*)-[(2-benzylidenecyclopropyl)methyl](phenyl)sulfane **2a** from (*E*)-2-(phenylmethylene)cyclopropylcarbinol **1a** via a substitution of its mesylated product with sodium benzenethiolate at

(1) For recent reviews, see: (a) Nakamura, I.; Yamamoto, Y. *Adv. Synth. Catal*. **2002**, *344*, 111. (b) Brandi, A.; Cicchi, S.; Cordero, F. M.; Goti, A. *Chem. Rev*. **2003**, *103*, 1213. (c) Nakamura, E.; Yamago, S. *Acc. Chem. Res*. **2002**, *35*, 867.

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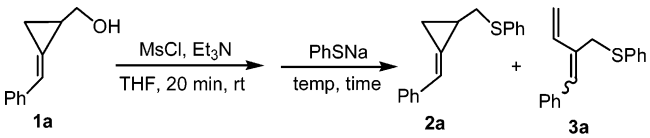
room temperature. However, we found that besides the desired product **2a**, a ring-opening concomitant, (2-benzylidenebut-3-enyl)(phenyl)sulfane **3a**, was also observed. This interesting observation stimulated us to examine this transformation in detail. These examinations using (*E*)-2-(phenylmethylene)-cyclopropylcarbinol (*E*)-**1a** as the substrate by converting (*E*)-**1a** to its mesylated intermediate through treatment with methanesulfonyl chloride and followed by the addition of sodium benzenethiolate as an nucleophile in a one-pot manner in a variety of solvents and under various conditions were aimed at determining the optimal conditions, and the results of these experiments are summarized in Table 1. We found that the in situ generated mesylated intermediate of **1a** reacted with sodium benzenethiolate in tetrahydrofuran (THF) at room temperature for 48 h to produce **2a** and **3a** (mixtures of *E*- and *Z*-isomers, $E/Z = 3/1$) in 41% and 25% yields, respectively (Table 1, entry 1). Upon heating under reflux in THF, the yield of **3a** was improved to 67% along with 11% of **2a** (Table 1, entry 2). Benzenethiol was not a suitable nucleophile for the formation of **2a** and **3a** (Table 1, entry 3). Products **2a** and **3a** could also be formed in good total yields in dichloromethane (DCM) and 1,2-dichloroethane (DCE) under reflux, but in lower selectivities (Table 1, entries 4−6). Using acetonitrile as a solvent gave lower total yields of **2a** and **3a** even upon heating under reflux (Table 1, entry 7). In refluxing toluene, **3a** was obtained exclusively in 41% yield within 6 h (Table 1, entry 8). The addition of water and sodium borohydride in THF dramatically increased the efficiency of the conversion of mesylated intermediate of **1a** to **2a** and **3a** at room temperature (20 °C), presumably because sodium borohydride could transform 1,2-diphenyldisulfane (PhSSPh), derived from the oxidation of sodium benzenethiolate during the reaction, to sodium benzenethiolate again[5] and water could increase the solubility of sodium benzenethiolate in the reaction mixture (Table 1, entry 9). It should be noted that in this case, **2a** was obtained as a major product. In addition, under these reaction conditions, 2.0 equiv of sodium benzenethiolate could give **2a** and **3a** in 50% and 6% yields, respectively (Table 1, entry 10).

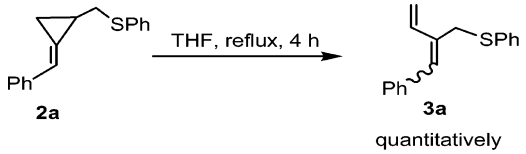
TABLE 1. Screening of the Reaction Conditions of 1a to Afford 2a and 3a



				yield[b] (%)	
entry[a]	solvent	temp (°C)	time (h)	**2a**	**3a** (*E*/*Z*)
1	THF	20	48	41	25 (3:1)
2	THF	70	24	11	67 (3:1)
3[c]	THF	20	24	trace	trace
4	DCE	20	20	51	<10 (3:1)
5	DCE	90	14	21	53 (3:1)
6	DCM	50	12	25	43 (3:1)
7	MeCN	90	24	19	34 (3:1)
8	PhMe	120	6		41 (3:1)
9[d]	THF	20	1	85	10 (3:1)
10[d,e]	THF	20	10	50	6 (3:1)

[a] All reactions were carried out with **1a** (0.30 mmol), MsCl (0.36 mmol), Et_3N (0.36 mmol), and PhSNa (0.90 mmol) in 2.0 mL of solvent under argon atmosphere except otherwise specified. [b] Isolated yields based on **1a**. [c] PhSH was used as the nucleophile. [d] Run with 20 equiv of H_2O and 2 equiv of $NaBH_4$ added. [e] Run with 2.0 equiv of PhSNa added.

SCHEME 1. Thermal-Induced Quantitative Transformation of 2a to 3a



Sequential investigation revealed that compound **2a** isolated as pure form by preparative TLC plates could be transformed quantitatively to the ring-opening product **3a** under reflux in THF for 4 h, indicating that compound **3a** was derived from product **2a** via a rearrangement rather than the attack of sodium benzenethiolate to the mesylated intermediate (Scheme 1). Therefore, the preparation of **3a** can be simplified by heating mixtures of **2a** and **3a**, synthesized under the conditions shown in entry 9 of Table 1, under reflux in THF within 4 h, affording **3a** as the sole product.

Following the simplified procedure, we next carried out the reactions with various 2-(arylmethylene)cyclopropylcarbinols **1** to examine the generality of this transformation. The results are summarized in Table 2. As can be seen from Table 2, for 2-(arylmethylene)cyclopropylcarbinols (*E*)-**1c**, (*E*)-**1e**, and (*E*)-**1h** having electron-donating groups on the benzene ring, the corresponding ring-opening products **3c**, **3e**, and **3h** were obtained in good to excellent yields (75−91%) as mixtures of *E*- and *Z*-isomers (Table 2, entries 3, 5, and 8). As for (*E*)-**1h**

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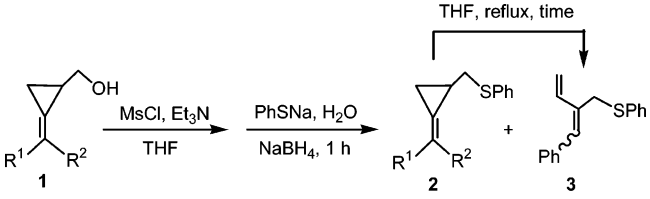
(4) (a) Shao, L.-X.; Li, Y.-X.; Shi, M. *Chem. Eur. J.* **2007**, *13*, 862. (b) Wang, B.-Y.; Huang, J.-W.; Liu, L.-P.; Shi, M. *Synlett* **2005**, 421. (c) Shi, M.; Wang, B.-Y. *Synlett* **2006**, 3158. (d) Shi, M.; Tian, G.-Q. *Tetrahedron Lett.* **2006**, *47*, 8059. (e) Tian, G.-Q.; Shi, M. *Org. Lett.* **2007**, *9*, 2405.

(5) Knapp, S.; Gibson, F. S. *J. Org. Chem.* **1992**, *57*, 4902.

TABLE 2. Transformation of 1 to the Ring-Opening Sulfanes 3



entry[a]	R^1/R^2	time (h)	yield[b] (%) **2**	yield[b] (%) **3** (*E*/*Z*)
1	C_6H_5/H, **1a**	4		**3a**, 96 (3:1)
2	4-BrC_6H_4/H, **1b**	3		**3b**, 92 (5:1)
3	4-MeC_6H_4/H, **1c**	7		**3c**, 75 (3:1)
4	4-ClC_6H_4/H, **1d**	20	**2d**, 42	**3d**, 53 (4;1)
5	4-MeOC_6H_4/H, **1e**	8		**3e**, 81 (3:1)
6	4-FC_6H_4/H, **1f**	15	**2f**, 61	**3f**, 37 (3:1)
7	2,4-$Cl_2C_6H_3$/H, **1g**	4		**3g**, 93 (5:1)
8	3,4,5-$(MeO)_3C_6H_2$/H, **1h**	*c*		**3h**, 91 (2:1)
9	H/C_6H_5, **1i**	8		**3a**, 94 (3:1)

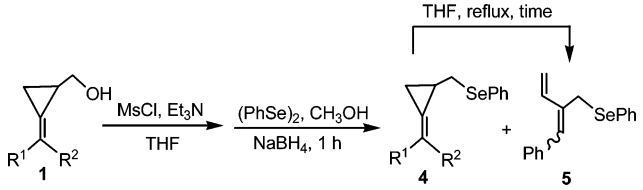
[a] All reactions were carried out with **1** (0.30 mmol), MsCl (0.36 mmol), and Et_3N (0.36 mmol) in 2.0 mL of THF under argon atmosphere, then PhSNa (0.90 mmol), H_2O (6.00 mmol), and $NaBH_4$ (0.90 mmol) were added after the mixture was stirred for 20 min at room temperature. [b] Isolated yields based on **1**. [c] At room temperature.

bearing three strongly electron-donating groups on the benzene ring, the reaction directly produced compound **3h** in 91% yield and the second step upon heating in THF is not required (Table 2, entry 8). As for 2-(arylmethylene)cyclopropylcarbinols (*E*)-**1d** and (*E*)-**1f** having moderately electron-withdrawing groups on the benzene ring, the corresponding ring-opening products **3d** and **3f** were obtained in lower yields (53% and 37%, respectively) as mixtures of *E*- and *Z*-isomers along with precursors **2d** and **2f** in moderate yields (42% and 61%), respectively, even under prolonged reaction time (Table 2, entries 4 and 6). These results indicate that electron-donating groups on the benzene ring favor this rearrangement. As for unsubstituted *E*-**1a**, *p*-bromosubstituted (*E*)-**1b**, and dichloro-substituted (*E*)-**1g**, these substrates could undergo substitution and rearrangement smoothly to afford products **3a**, **3b**, and **3g** in excellent yields (96%, 92%, and 93%) as mixtures of *E*- and *Z*-isomers, respectively (Table 2, entries 1, 2, and 7). For (*Z*)-2-(phenylmethylene)cyclopropylcarbinol, this reaction could also take place smoothly to furnish the same product **3a** as that from (*E*)-**1a** as mixtures of *E*- and *Z*-isomers (Table 2, entry 9).

Similarly, the in situ generated selenides **4**, which were prepared via a substitution of mesylated intermediates of **1** by sodium benzeneselenolate derived from 1,2-diphenyldiselane with sodium borohyride and methanol,[5] could also undergo the same type of rearrangement to give the corresponding ring-opening products **5** in good yields. The results are summarized in Table 3. As can be seen from Table 3, the reactions proceeded more smoothly than those of sulfides. As for 2-(arylmethylene)-cyclopropylcarbinols **1**, whether having electron-donating groups or electron-withdrawing ones on the benzene ring, the ring-opening products (2-arylmethylidenebut-3-enyl)(phenyl)selanes **5** were obtained in good to excellent yields within shorter reaction time (Table 3, entries 1−7).[6] As for 3,4,5-trimethoxy groups substituted **1h**, the substitution of mesylated intermediate of **1h** by sodium benzeneselenolate took place immediately to produce product **5h** in good yield at room temperature (20 °C),

(6) Since compound **4** can be easily converted to product **5**, we did not isolate any compound **4** as pure form.

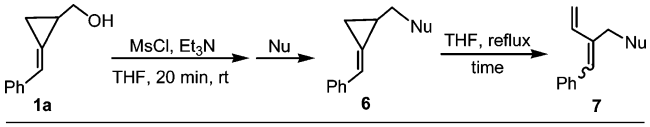
TABLE 3. Transformation of 1 to the Ring-Opening Selanes 5



entry[a]	R^1/R^2	time (h)	yield[b] (%) 4	yield[b] (%) **5** (*E*/*Z*)
1	C_6H_5/H, **1a**	1		**5a**, 97 (3:1)
2	4-BrC_6H_4/H, **1b**	3		**5b**, 74 (5:1)
3	4-MeC_6H_4/H, **1c**	2		**5c**, 92 (3:1)
4	4-ClC_6H_4/H, **1d**	2		**5d**, 99 (2;1)
5	4-MeOC_6H_4/H, **1e**	2		**5e**, 96 (2:1)
6	4-FC_6H_4/H, **1f**	12		**5f**, 89 (2:1)
7	2,4-$Cl_2C_6H_3$/H, **1g**	2		**5g**, 88 (3:1)
8	3,4,5-$(MeO)_3C_6H_2$/H, **1h**	0		**5h**, 87 (2:1)
9	H/C_6H_5, **1i**	1.5		**5a**, 75 (3:1)
10	H/4-MeOC_6H_4, **1j**	2		**5e**, 96 (2:1)

[a] All reactions were carried out with **1** (0.30 mmol), MsCl (0.36 mmol), and Et_3N (0.36 mmol) in 2 mL of THF under argon atmosphere, then $(PhSe)_2$ (0.60 equiv), CH_3OH (3.00 mmol) and $NaBH_4$ (0.90 mmol) were added after the mixture was stirred for 20 min at room temperature. [b] Total isolated yields

TABLE 4. Effects of Heating Halide Derivatives from 1



entry[a]	Nu	time (h)	yield[b] (%) **6**	yield[b] (%) **7**
1	NaCl	24	**6i**, 94	
2	LiBr	12	**6j**, 77	
3	NaI	12	**6m**, 81[c]	**7m**, 14

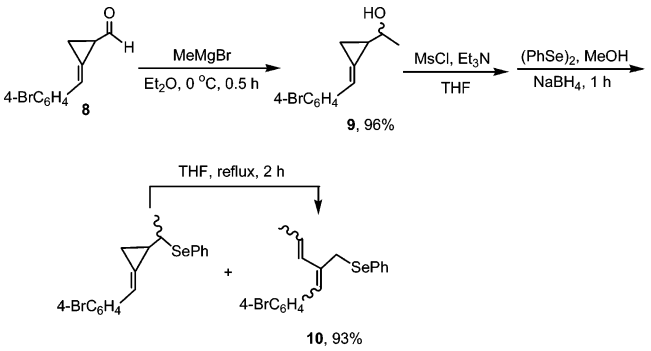
[a] All reactions were carried out with **1a** (0.30 mmol), MsCl (0.36 mmol), Et_3N (0.36 mmol), nucleophiles(0.90 mmol) and 2.0 mL of solvent under argon atmosphere. [b] Isolated yields. [c] Mixtures of *Z*- and *E*-isomers (1:1).

and therefore the heating in THF was not required, suggesting again that electron-donating groups on the benzene ring favor this rearrangement (Table 3, entry 8). *Z*-2-(Arylmethylene)-cyclopropylcarbinols could also produce the corresponding rearrangement products in high yields (Table 3, entries 9 and 10).

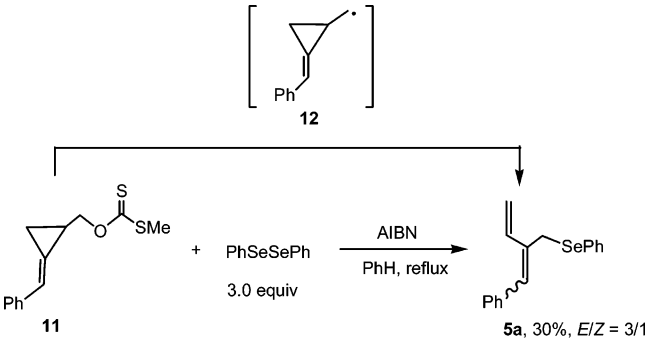
Halide ions have been considered as good nucleophiles for mesylated intermediate of **1**. However, we found that the corresponding chlorinated and brominated compounds **6i** and **6j** were formed without formation of the corresponding ring-opening products **7** under the standard conditions (Table 3, entries 1 and 2). As for sodium iodide, the expected iodide **7m** was obtained in 14% yield along with iodinated product **6m** as a major product, suggesting that the halogenated products **6** cannot undergo such rearrangement efficiently (Table 4, entries 1−3).

To ascertain the pathway of this rearrangement, compound **9** was synthesized by addition of methylmagnesium bromide to compound **8** to label the hydroxylated carbon. Under the optimal reaction conditions, compound **9** could be transformed to the ring-opening product **10** with the newly formed carbon−carbon double bond positioned on the labeled carbon (Scheme 2).

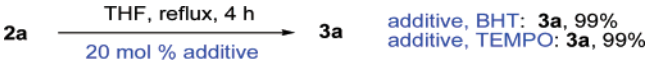
SCHEME 2. Transformation with Secondary Alcohol



SCHEME 3. Formation of 5a via a Radical Process

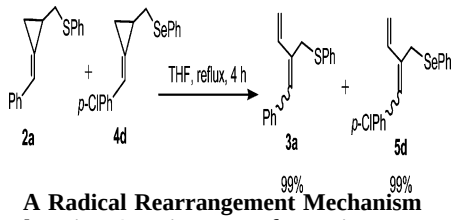


SCHEME 4. Control Experiment for This Radical Transformation

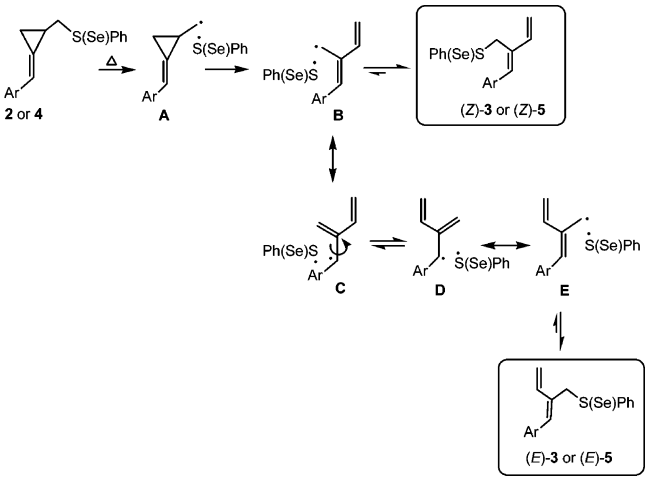


Moreover, to further clarify the reaction mechanism, we synthesized dithiocarbonic acid *O*-(2-benzylidene-cyclopropylmethyl) ester *S*-methyl ester **11** for a control experiment since this compound could readily undergo deoxygenation to form a radical **12** initiated by 2,2′-azobisisobutyronitrile (AIBN) upon heating (Scheme 3).[7] Indeed, it was found that compound **5a** was produced in 30% yield as mixtures of *E*- and *Z*-isomers when compound **11** was treated with 1,2-diphenyldiselane (3.0 equiv) and AIBN (5.0 mol %) under reflux in benzene for 2 days (Scheme 3). This result indicated that the transformation of **2** or **4** to **3** or **5** might proceed via a radical process.[8] It should be noted here that the control experiment has confirmed that this intramolecular radical rearrangement under the optimized conditions was unaffected by the addition of the radical inhibitors such as 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) and 2,6-di-*tert*-butyl-4-methylphenol (BHT) (20 mol %), presumably because these radical inhibitors are unable to affect such rapid intramolecular radical rearrangement (Scheme 4). Another crossover experiment was performed using **2a** and **4d** under the standard conditions. The result is presented in Scheme 5. It was found that the scrambling products were not formed under the reaction conditions, suggesting again that this intramolecular radical pair rearrangement is very fast.

SCHEME 5. Crossover Experiment Using 2a and 4d under the Standard Conditions



SCHEME 6. A Radical Rearrangement Mechanism Proposed for the Ring-Opening Transformation



According to above results, a radical pair rearrangement mechanism is outlined in Scheme 6. First, compound **2** or **4** undergoes thermal homolysis to produce radical pair **A**, which delivers allylic radical pair **B** via a cyclopropane ring-opening process.[9] At this moment, (*Z*)-**3** or (*Z*)-**5** could be produced by the recombination of radical pair **B**. On the other hands, allylic radical pair **C** can be formed from radical pair **B** through allylic rearrangement, which gives another allylic radical pair **D** via rotation across the single bond. Subsequent similar allylic rearrangement produces allylic radical pair **E**, which furnishes the favored isomers (*E*)-**3** or (*E*)-**5** through recombination. The selectivity may simply come from the more thermodynamically stable *E*-isomers than *Z*-isomers owing to the steric factors. On the other hand, an ionic process could also account for this transformation and we could not exclude this mechanism at present stage.

In conclusion, we have developed an interesting procedure for the preparation of (2-arylmethylidenebut-3-enyl)(phenyl)-sulfanes **3** and (2-arylmethylidenebut-3-enyl)(phenyl) selanes **5** from the reaction of 2-(arylmethylene)cyclopropylcarbinols **1** with sodium benzenethiolate and sodium benzeneselenolate in good to excellent yields via simple operation under mild conditions. A radical pair rearrangement mechanism accounting for the cyclopropane ring-opening and allylic isomerization has been proposed. Further studies regarding the mechanistic details and scope of this process are in progress.

Experimental Section

General Procedure for the Preparation of (2-Arylmethylidenebut-3-enyl)(phenyl)sulfanes. To a solution of (*E*)- or (*Z*)-2-(arylmethylene)cyclopropylcarbinols **1** (0.30 mmol in 1.0 mL of

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tetrahydrofuran) were added triethylamine (0.36 mmol) and methanesulfonyl chloride (0.36 mmol) under argon atmosphere. The reaction mixtures were stirred at room temperature for 20 min, then sodium benzenethiolate (0.90 mmol), sodium borohydride (0.60 mmol), and water (6.00 mmol) were added. Then, the mixtures of **2** and **3** were heated under reflux in tetrahydrofuran (THF). After the transformation was completed on the basis of TLC plates, the solvent was removed under reduced pressure and the residue was purified by silica gel column chromatograph to afford the pure products **3**.

General Procedure for the Preparation of (2-Arylmethylidenebut-3-enyl)(phenyl)selanes. To a solution of 2-(arylmethylene)cyclopropylcarbinols **1** (0.30 mmol in 1.0 mL of tetrahydrofuran) were added triethylamine (0.36 mmol) and methanesulfonyl chloride (0.36 mmol) under argon atmosphere. The mixtures were stirred at room temperature for 20 min, then 1,2-diphenyldiselane (0.60 mmol) and sodium borohydride (0.90 mmol) were added. After stirring for a given time, mixtures of {[(2-arylmethylene)-cyclopropyl]methyl}(phenyl)selanes **4** or (2-arylmethylidenebut-3-enyl)(phenyl)selanes **5** were isolated. Then, the mixtures of **4** and **5** were heated under reflux in tetrahydrofuran. After the transformation completed on the basis of TLC plates, the solvent was removed under reduced pressure and the residue was purified by silica gel column chromatograph to afford the pure products **5**.

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Supporting Information Available: The spectroscopic data of the new compounds and the detailed description of experimental procedures. This material is available free of charge via the Internet at http://pubs.acs.org.

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