

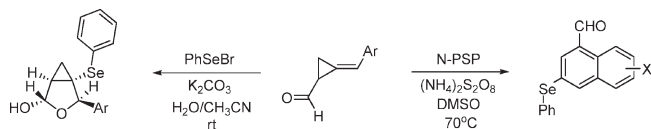
**Organo-Selenium Induced Radical Ring-Opening  
Intramolecular Cyclization or Electrophilic  
Cyclization of 2- (Arylmethylene)  
cyclopropylaldehyde: A Tunable Synthesis of  
1-Naphthaldehydes or 3-Oxabicyclo[3.1.0]hexan-2-ols**

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1-Naphthaldehydes and 3-oxabicyclo[3.1.0]hexan-2-ols can be prepared, respectively, by the intramolecular alkylation and cyclization of (*E*)-2-(arylmethylene)cyclopropylaldehyde **1** mediated by different organo-selenium reagents. The properties of selenium reagents may play an important role in the reactions. A rationale for these transformations is proposed.

Methylenecyclopropanes (MCPs), which are highly strained but readily accessible carbocyclic molecules, have been extensively studied and are usually employed for the construction of

complex and interesting organic molecules.<sup>1</sup> In the past decades, much attention has been paid to the transition metal<sup>2</sup> and Lewis acid<sup>3</sup> catalyzed reactions of MCPs through three different reaction pathways, namely, addition to C=C bond, distal, and proximal C–C bond cleavages. A troublesome feature of unfunctional MCPs is their multiform reactivities that may lead to formation of a variety of products.

Recently, MCPs with functional groups attached to a cyclopropyl ring have received considerable attention.<sup>4</sup> Ma previously reported a highly selective ring-opening cycloisomerization of methylene- or alkylidenecyclopropyl ketones catalyzed by Pd(II) catalyst,<sup>4a</sup> and Lautens has shown a novel ring expansion of secondary methylenecyclopropyl amides in the presence of MgI<sub>2</sub>,<sup>4c</sup> leading to useful compounds with synthetic and biological importance. Wang has presented the Friedel–Crafts reaction initiated by the direct generation of a carbocation at the C3 position of MCP 1,1-diester through distal bond cleavage.<sup>4c</sup> Recently, we reported substrate-controlled selective proximal and distal C–C bond cleavage via Lewis acid mediated O-acylation of 2-(arylmethylene)cyclopropylaldehyde.<sup>4f</sup> In principle, the presence of functional groups may facilitate the selective cleavage of C–C bonds of MCPs, thus delicately tuning the regioselectivity of the reactions.

Organo-selenium compounds are now commonly employed as very useful and powerful reagents, which allow the chemo-, regio-, and stereoselective introduction of new functional groups into complex organic substrates.<sup>5</sup> Selenium can be introduced as an electrophile, a nucleophile, or a radical.<sup>6</sup> Shi and we have disclosed the reactions of MCPs with various selenium reagents to afford useful selenium-containing compounds.<sup>7</sup> In this paper, we wish to report an organo-selenium promoted reaction of formyl-substituted MCPs, providing a selective synthesis of 1-naphthaldehydes and 3-oxabicyclo[3.1.0]hexan-2-ols.

Initially, the reaction of (*E*)-**1a** and diphenyl diselenide was performed in the presence of K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> in CH<sub>3</sub>CN at 70 °C,

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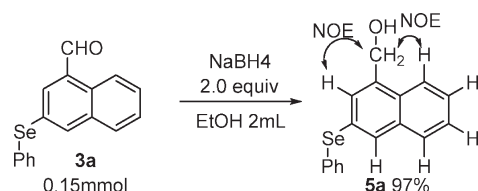
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TABLE 1. Reaction of (*E*)-1a with Various Selenium Reagents under Different Conditions<sup>a</sup>

entry	selenium reagents (equiv)	temp (°C)	solvent	time (min) <sup>b</sup>	yield (%) <sup>c</sup>
1	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub> (1.5) PhSeSePh (0.5)	70	CH <sub>3</sub> CN	20	26
2	(NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>8</sub> (1.5) PhSeSePh (0.5)	70	CH <sub>3</sub> CN	20	47
3	(NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>8</sub> (1.5) PhSeSePh (0.5)	reflux	THF	30	NR <sup>d</sup>
4	(NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>8</sub> (1.5) PhSeSePh (0.5)	70	DMSO	5	55
5	(NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>8</sub> (1.0) N-PSP (1.2)	70	DMSO	5	61
6	(NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>8</sub> (1.0) N-PSP (1.2)	45	DMSO	5	52
7	(NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>8</sub> (1.0) N-PSP (1.2)	100	DMSO	5	21
8	(NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>8</sub> (1.0) PhSeBr (1.2)	70	DMSO	10	trace
9	(NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>8</sub> (1.0) PhSeCl (1.2)	70	DMSO	30	trace

<sup>a</sup>Unless otherwise specified, the reaction was carried out using (*E*)-1a (0.2 mmol) in 3 mL of solvent at N<sub>2</sub> atmosphere. <sup>b</sup>The reaction was monitored by TLC. <sup>c</sup>Isolated yields. <sup>d</sup>No reaction.

SCHEME 1. Establishment of the Structure of 3a



affording 3-(phenylselenenyl)-1-naphthaldehyde (**3a**) in 26% (Table 1, entry 1). The structure of **3a** was established by the NOESY analysis of **5a**, which was reduced by treatment of **3a** with NaBH<sub>4</sub> (Scheme 1). Using (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> instead of K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> led to the increased yield of 47% (Table 1, entry 2). The yield could be further improved to 55% when the reaction was conducted in DMSO (Table 1, entry 4). Screen of the selenium reagents proved that the use of *N*-(phenylseleno) phthalimide (N-PSP) gave better results than diphenyl diselenide (Table 1, entry 5). Phenylselenenyl bromide and phenylselenenyl chloride were totally ineffective for this reaction (Table 1, entries 8 and 9).

With the optimized conditions in hand, we next probed the reaction of a variety of (*E*)-1 with N-PSP, and the experimental results showed that the corresponding adducts **3** were obtained in moderate yields. The yields of the (*E*)-1a with electron-donating groups on the aromatic rings appear to be higher than those with electron-withdrawing groups (Table 2, entries 1–8). In the synthesis of (*E*)-1a, a small amount of (*Z*)-1a isomer was obtained. The reaction of (*Z*)-1a with N-PSP gave the same product (Table 2, entry 10).

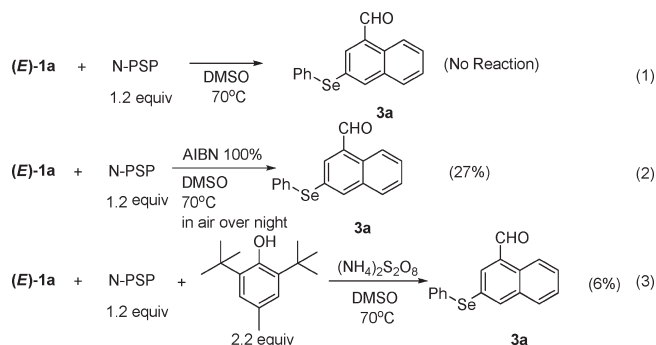
Phenylselenenyl bromide and phenylselenenyl chloride are a class of typical phenylselenenyl cation sources and have wide application in the electrophilic addition reaction.<sup>8</sup> However, as indicated in Table 1, when phenylselenenyl bromide and phenylselenenyl chloride were used, the reaction of (*E*)-1a only gave a trace amount of the expected product, which may

TABLE 2. Reaction of (*E*)-1 with N-PSP

entry <sup>a</sup>	Ar <sup>1</sup>	Ar <sup>2</sup>	products	yield (%) <sup>b</sup>
1	Ph	Ph	<b>3a</b>	61
2	<i>p</i> -MePh	Ph	<b>3b</b>	73
3	<i>p</i> -OMePh	Ph	<b>3c</b>	80
4	<i>p</i> -ClPh	Ph	<b>3d</b>	56
5	<i>p</i> -BrPh	Ph	<b>3e</b>	39
6	<i>p</i> -FPh	Ph	<b>3f</b>	53
7	<i>o</i> -BrPh	Ph	<b>3g</b>	42
8	<i>o</i> -OMePh	Ph	<b>3h</b>	45
9	Ph	<i>p</i> -MePh	<b>3i</b>	67
10	Ph	Ph	<b>3a</b>	42 <sup>c</sup>

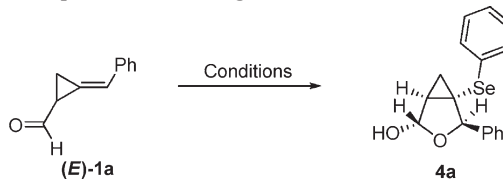
<sup>a</sup>Unless otherwise specified, the reaction was carried out using (*E*)-1 (0.2 mmol), N-PSP (0.24 mmol) in 3 mL of DMSO at N<sub>2</sub> atmosphere. <sup>b</sup>Isolated yields. <sup>c</sup>(*Z*)-1a was applied to this reaction.

SCHEME 2. Controlled Experiments



exclude the cation process. The reaction of (*E*)-1a and N-PSP did not occur with no (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> added (eq 1, Scheme 2). On the other side, when the reaction was carried out in the

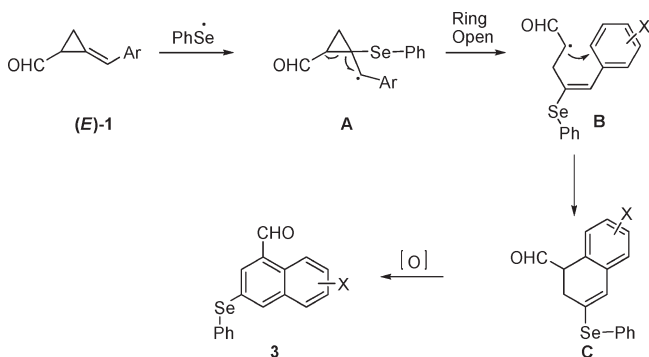
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TABLE 3. Reaction of (*E*)-1a with Various Electrophilic Selenium Reagents under Different Conditions<sup>a</sup>


entry	electrophilic selenium reagents (equiv)	solvent	base	yield (%) <sup>c</sup>
1	PhSeCl (1.2)	DMSO + 0.1 mL H <sub>2</sub> O		61
2	PhSeBr (1.2)	DMSO + 0.1 mL H <sub>2</sub> O		66
3	PhSeBr (1.2)	CH <sub>3</sub> CN + 0.1 mL H <sub>2</sub> O		73
4	PhSeBr (1.2)	CH <sub>2</sub> Cl <sub>2</sub> + 0.1 mL H <sub>2</sub> O		46
5	PhSeBr (1.2)	CH <sub>3</sub> CN + 0.1 mL H <sub>2</sub> O	K <sub>2</sub> CO <sub>3</sub>	<b>89</b>
6	PhSeBr (1.2)	CH <sub>3</sub> CN + 0.2 mL H <sub>2</sub> O	K <sub>2</sub> CO <sub>3</sub>	85
7	PhSeBr (1.2)	CH <sub>3</sub> CN + 0.01 mL H <sub>2</sub> O	K <sub>2</sub> CO <sub>3</sub>	61
8	N-PSP (1.2)	CH <sub>3</sub> CN + 0.1 mL H <sub>2</sub> O	K <sub>2</sub> CO <sub>3</sub>	NR <sup>d</sup>

<sup>a</sup>Unless otherwise specified, the reaction was carried out using (*E*)-1a (0.2 mmol) in 3 mL of solvent. <sup>b</sup>Reaction was monitored by TLC. <sup>c</sup>Isolated yields. <sup>d</sup>No reaction.

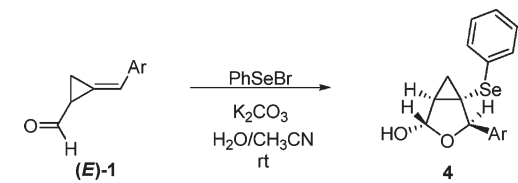
SCHEME 3. Proposed Mechanism for the Reaction



presence of 1.0 equiv of 2,2'-azo-bis-isobutyronitrile (AIBN) and air, the corresponding product was also formed in 27% yield (eq 2, Scheme 2), albeit in low yield with long reaction time, comparatively. When radical inhibitor was added in the reaction system, the yield of **3a** significantly dropped to 6% (eq 3, Scheme 2). These results may indicate that the radical process may be the main pathway in this reaction.

On the basis of the above results, a plausible mechanism was proposed, as shown in Scheme 3. The reaction of N-PSP with free radical initiator (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub><sup>9</sup> may first give the phenylselenenyl radical, which adds to the C=C bond of (*E*)-1 to produce the radical intermediate **A**. The presence of a formyl group may facilitate a highly selective scission of the proximal C–C bond in the cyclopropane ring to afford intermediate **B**, followed by the intramolecular radical cyclization reaction to give 1,2-dihydronaphthalene **C** with loss of a hydrogen atom. Finally, 1,2-dihydronaphthalene **C** is oxidized by (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> to give the more stable 1-naphthaldehyde derivative **3**.

Interestingly, when the reaction was conducted in 3 mL of DMSO and 0.1 mL of H<sub>2</sub>O using phenylselenenyl chloride as the electrophilic selenium reagents, the bicycle derivatives 3-oxabicyclo[3.1.0]hexan-2-ols **4a** were obtained in 61%

TABLE 4. Reaction of (*E*)-1a with H<sub>2</sub>O in the Presence of Phenylselenenyl Bromide


entry <sup>a</sup>	Ar	products	yield (%) <sup>b</sup>
1	Ph	<b>4a</b>	89
2	<i>p</i> -BrPh	<b>4b</b>	86
3	<i>p</i> -MePh	<b>4c</b>	91
4	<i>p</i> -OMePh	<b>4d</b>	75
5	<i>p</i> -ClPh	<b>4e</b>	88
6	<i>o</i> -BrPh	<b>4f</b>	79

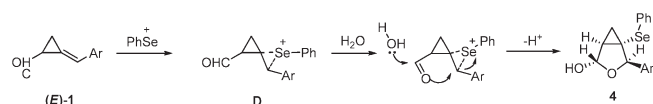
<sup>a</sup>Unless otherwise specified, the reaction was carried out using (*E*)-1 (0.2 mmol), PhSeBr (0.24 mmol), and K<sub>2</sub>CO<sub>3</sub> (0.24 mmol) in 3 mL of CH<sub>3</sub>CN and 0.1 mL of H<sub>2</sub>O in an air atmosphere. <sup>b</sup>Isolated yields.

yield with excellent stereoselectivity (Table 3, entry 1). Using (*E*)-1a as the substrate, we examined the reaction under a variety of reaction conditions to develop the best one. The results are summarized in Table 3. Using phenylselenenyl bromide instead of phenylselenenyl chloride led to the increased yield of 66% (Table 3, entry 2). The following examination of the solvent effects indicated that CH<sub>3</sub>CN was the most suitable solvent (Table 3, entries 2–4). When the base K<sub>2</sub>CO<sub>3</sub> was used in CH<sub>3</sub>CN, **4a** was obtained in 89% yield (Table 3, entry 5). Moreover, the amount of H<sub>2</sub>O also affected the yield of the reaction, and 0.1 mL of H<sub>2</sub>O is suitable (Table 3, entries 5–7). Thus, the optimized conditions are to carry the reaction in 3 mL of CH<sub>3</sub>CN and 0.1 mL of H<sub>2</sub>O using 1.2 equiv of phenylselenenyl bromide and 1.2 equiv of K<sub>2</sub>CO<sub>3</sub> at room temperature. When the selenium reagent N-PSP was used instead of phenylselenenyl bromide, no reaction occurred (Table 3, entry 8).

With the optimized reaction conditions in hand, we next examined the electrophilic cycloaddition of a variety of (*E*)-1 with phenylselenenyl bromide. The results are shown in Table 4. The positions and properties of substituents on the aromatic ring of (*E*)-1 have little effect on the reaction, and the

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## SCHEME 4. Proposed Mechanism for the Reaction



products **4** were obtained in good to high yields (Table 4, entries 1–6). Here, it should be mentioned that oxabicyclo[3.1.0]hexan-2-ols are important structural motifs frequently found in pharmacologically interesting structures.<sup>10</sup>

Obviously, the reaction mechanism in CH<sub>3</sub>CN and H<sub>2</sub>O is different from that in dry DMSO. In the CH<sub>3</sub>CN and H<sub>2</sub>O system, the phenylselenium first adds to the double bonds to form a seleniranium ion intermediate **D**. Then a molecule of H<sub>2</sub>O nucleophilically attacks at the carbonyl group of the intermediate **D**, and simultaneously, the oxygen in the carbonyl group undergoes intramolecular nucleophilic attack to form the bicycle derivatives **4** with excellent stereoselectivity (Scheme 4).

In summary, we have observed a ring-opening intramolecular radical cyclization and an electrophilic cyclization reaction of 2-(arylmethylene)cyclopropylaldehyde, affording a controlled synthesis of 1-naphthaldehydes and 3-oxabicyclo[3.1.0]hexan-2-ols from (*E*)-2-(arylmethylene)cyclopropylaldehyde. The properties of organo-selenium reagents may play an important role in the reactions. Further studies on this transformation are being carried out in our laboratory.

## Experimental Section

General Procedure for Synthesis of 1-Naphthaldehydes **3**.

Under an atmosphere of dry nitrogen, 1.0 equiv of (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (0.2 mmol) was added to a solution of N-PSP (0.24 mmol) in 3 mL of dry DMSO at 70 °C. Then 1.0 equiv of (*E*)-**1** (0.2 mmol) was added. After being stirred for 5–20 min (monitored by TLC), the mixture was quenched with 5 mL of water and extracted with EtOAc (3 × 10 mL). The combined organic layers were dried over anhydrous MgSO<sub>4</sub>. After filtration and removal of the solvent in vacuo, the residues were purified

with flash chromatography on silica gel (petroleum ether/ethyl acetate 50:1 v/v) to afford **3**.

**3-Phenylselanyl-naphthalene-1-carbaldehyde (3a):** oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ = 10.26 (s, 1H), 9.17 (d, *J* = 8.0 Hz, 1H), 8.17 (s, 1H), 7.98 (d, *J* = 1.6 Hz, 1H), 7.79 (d, *J* = 8.4 Hz, 1H), 7.68–7.70 (m, 1H), 7.50–7.60 (m, 3H), 7.29–7.35 (m, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ = 124.9, 127.5, 127.8, 127.9, 128.0, 129.1, 129.3, 129.6, 130.0, 132.0, 133.3, 134.4, 138.3, 140.5, 192.9; IR (neat) 1689, 1617, 1574, 1501, 1214, 1061, 736, 689 cm<sup>-1</sup>; MS (70 eV, EI) *m/z* 312 (M<sup>+</sup>); HRMS (EI) *m/z* calcd for C<sub>17</sub>H<sub>12</sub>OSe (M<sup>+</sup>) 312.0053, found 312.0048.

**General Procedure for Synthesis of 3-Oxabicyclo[3.1.0]hexan-2-ols **4**.** To a stirred solution of (*E*)-**1** (0.2 mmol) in CH<sub>3</sub>CN (3 mL) was added 0.1 mL of H<sub>2</sub>O and K<sub>2</sub>CO<sub>3</sub> (0.24 mmol) at room temperature, then the PhSeBr (0.24 mmol) was added. After the reaction was complete (20 min), the mixture was quenched with 5 mL of water and extracted with EtOAc (3 × 5 mL). The combined organic layers were dried over anhydrous MgSO<sub>4</sub>. After filtration and removal of the solvent in vacuo, the residues were purified with flash silica chromatography (petroleum ether/ethyl acetate 6:1 v/v) to afford **4**.

**4-Phenyl-5-phenylselanyl-3-oxabicyclo[3.1.0]hexan-2-ol (4a):** oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ = 7.38–7.46 (m, 4H), 7.28–7.33 (m, 3H), 7.16–7.22 (m, 3H), 5.42 (d, *J* = 1.6 Hz, 1H), 5.32 (s, 1H), 3.05–3.18 (m, 1H), 2.05 (dd, *J*<sub>1</sub> = 4.4 Hz, *J*<sub>2</sub> = 8.4 Hz, 1H), 1.19–1.23 (m, 1H) 1.00–1.06 (m, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ = 13.8, 29.7, 32.9, 81.5, 98.0, 126.7, 127.2, 128.0, 128.1, 129.0, 129.3, 132.2, 137.3; IR (neat) 3396, 1468, 1086, 1060, 962, 816, 733, 689 cm<sup>-1</sup>; MS (70 eV, EI) *m/z* 332 (M<sup>+</sup>); HRMS (EI) *m/z* calcd for C<sub>17</sub>H<sub>16</sub>O<sub>2</sub>Se (M<sup>+</sup>) 332.0316, found 332.0312.

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**Supporting Information Available:** General experimental procedures and spectroscopic data for all compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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