

# Formation of a Sterically Crowded 1,6,6 $\alpha\lambda^4$ -Triselenapentalene and 4*H*-Selenopyran-4-selones Fused with Two Bornane Skeletons Through the Reaction of *d*-Camphor *p*-Toluenesulfonylhydrazone With a Base and Elemental Selenium

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## Abstract

Reaction of *d*-camphor *p*-toluenesulfonylhydrazone with *t*-butoxide and elemental selenium in dimethylformamide at an elevated temperature afforded a stable compound having a unique 1,6,6 $\alpha\lambda^4$ -triselenapentalene ring and 4*H*-selenopyran-4-selones along with dialkenyl diselenide, dibornylenes, and 1,2,5-triselenepin, and the structural confirmation of these products were carried out by X-ray crystallographic analysis. The sterically crowded 1,6,6 $\alpha\lambda^4$ -triselenapentalene ring fused with two bornane skeletons was stable enough under aerobic exposure and was inactive toward sodium borohydride reduction but was converted into 1,2-diselenole derivative through *m*-chloroperbenzoic acid oxidation.

## Keywords

*d*-camphor*p*-toluenesulfonylhydrazone, 1,6,6 $\alpha\lambda^4$ -triselenapentalene, 4*H*-selenopyran-4-selone, steric protection, 1,2-diselenole

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Dialkenyl dichalcogenides have been widely recognized as the versatile synthetic precursors of various chalcogen-containing heterocycles and chalcogenocarbonyl compounds,<sup>1–9</sup> and the recent synthetic interests have been concentrated to their higher-row derivatives. However, in spite of the potentiality of alkeneselenolate and alkenetelluroate ions as the synthetic equivalents of selenocarbonyl and tellurocarbonyl compounds,<sup>10–17</sup> only limited studies on the generation of these alkenechalcogenolate ions have been carried out previously and the lack of general and convenient synthetic methods of these compounds has restrained the extension on the novel conversion of these compounds into chalcogen-containing heterocyclic compounds. In the course of our successive studies on the synthesis of higher-row chalcogenocarbonyl compounds, we have found a convenient synthesis of dialkenyl diselenides **C** through the reaction of *p*-toluenesulfonylhydrazones **A**, derived from ketones possessing an  $\alpha$ -methylene group, with a base and elemental selenium.<sup>18–24</sup> The reaction was assumed to proceed through the in situ generated alkeneselenolate ions **B** via Bamford–Stevens type reaction of *p*-toluenesulfonylhydrazones<sup>25–33</sup> as shown in Scheme 1, and, therefore, the synthetic application of this sequence to the

preparation of various selenium-containing heterocyclic compounds was keenly expected.

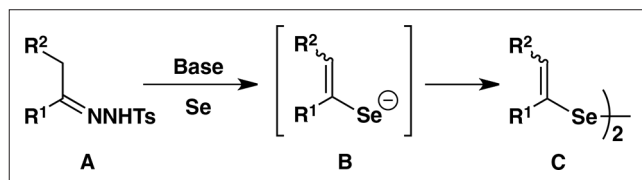
Especially, our interests have been concentrated to the application of the reaction sequence by using the bornane derivatives because *d*-camphor and its functionalized derivatives have been widely recognized as the versatile substrates for chiral auxiliaries, chiral ligands, and chiral building blocks for asymmetric syntheses due to their commercial availability with the structural stability and its chirality.<sup>34–37</sup> However, in spite of the extensive research works on the functionalization of bornane skeletons within these decades, there found only limited studies on the selenium-functionalized bornane skeletons except for our previous works on the preparation and the conversion of substituted bornane-2-selones. Our previous

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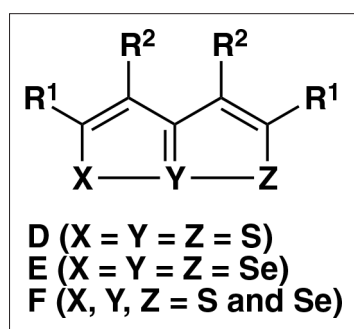




**Scheme 1.** Synthesis of dialkenyl diselenides **C** via the reaction of ketone *p*-toluenesulfonylhydrazone with a base and elemental selenium.

attempts for the synthesis of dibornenyl diselenide using our procedure starting from *d*-camphor *p*-toluenesulfonylhydrazone (**1**) also resulted in the complex mixture containing dibornylene (**3**), 1,4-diselenin (**4**), 1,2,5-triselenepin (**5**), and a few uncharacterized compounds along with the formation of dibornenyl diselenide (**2**).<sup>18</sup> Therefore, we just started the investigation of the structural confirmation of these uncharacterized byproducts in order to obtain a key for the optimization of the reaction conditions, and after several efforts, we could isolate and characterize the structures of some of these byproducts involving a hitherto unknown purple-colored stable crystalline compounds, 1,6,6 $\alpha$ ^4-triselenapentalene (**6**), and an isomeric mixture of greenish brown-colored 4*H*-selenopyran-4-selones (**7**, **8**) fused with two bornane skeletons.

1,6,6 $\alpha$ ^4-Triselenapentalenes **D** and their oxygen or nitrogen analogs are classified to be bicyclic 10-S-3 type sulfuranes having three sulfur atoms with a central hypervalent sulfur atom in the heteroaromatic ring system, and their structures, chemical reactivity, and their synthetic methods have been extensively investigated during these decades.<sup>38-50</sup> However, in contrast to 1,6,6 $\alpha$ ^4-trithiapentalenes **D**, only a few synthetic studies on their selenium analogs, such as 1,6,6 $\alpha$ ^4-triselenapentalenes **E**,<sup>51-55</sup> 1,6,6 $\alpha$ ^4-thiadiselenapentalenes, and 1,6,6 $\alpha$ ^4-dithiaselenapentalenes **F**,<sup>56-58</sup> have been carried out to date may be due to the difficulty in the preparation of suitable 1,3,5-triselenoxo intermediates. The general structures of compounds **D-F** are shown in Figure 1. In this report, we would like to describe the isolation and characterization of new 1,6,6 $\alpha$ ^4-triselenapentalene (**6**) and 4*H*-selenopyran-4-selones



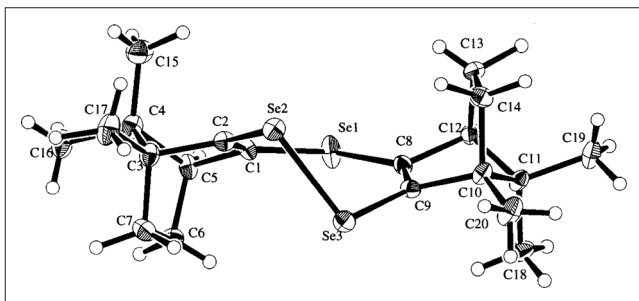
**Figure 1.** Structures of 1,6,6 $\alpha$ ^4-trichalcogenapentalenes **D**, **E**, and **F**.

(**7**, **8**) fused with two bornane skeletons as the minor products of the reaction of *d*-camphor *p*-toluenesulfonylhydrazone (**1**) with *t*-butoxide (*t*-BuOK) and elemental selenium at an elevated temperature. A novel oxidative selenium-oxygen replacement of **6** forming 1,2-diselenole (**11**) bearing a neighboring carbonyl group is also reported in this paper.

*d*-Camphor was at first converted into the corresponding *p*-toluenesulfonylhydrazones (**1**) according to the usual procedure. Subsequently, a hexamethylphosphoric triamide (HMPA) or a dimethylformamide (DMF) solution of *d*-camphor *p*-toluenesulfonylhydrazone (**1**) was treated with *t*-BuOK (2.5 mol amt.) and elemental sulfur or selenium (2.5 mol amt.) at 110°C-140°C for 3-24 hours followed by an aerobic exposure of the resulting reaction mixture at room temperature,<sup>18</sup> and only in the cases using elemental selenium, small amounts of several selenium-containing products were isolated besides dialkenyl diselenide (**2**), an *E,Z*-mixture of dimeric olefins (**3**),<sup>59,60</sup> and a few uncharacterized products. On the other hand, the same reactions performed at a higher temperature over 160°C only afforded a complex mixture, and the similar reaction using elemental sulfur only afforded a complex mixture.

The mixture of less polar selenium-containing products obtained as orange oil gradually underwent decomposition with selenium extrusion during the workup procedure to form a separable mixture of relatively stable two compounds, pale yellow solids, and orange solids. All physical and spectral data for the former and the latter compound, involving mass spectrometry (MS), infrared (IR), <sup>1</sup>H nuclear magnetic resonance (NMR), <sup>13</sup>C NMR, and elemental analysis, were fully consistent with 1,2- or 1,4-diselenin (**4**) and symmetrical 1,2,5-triselenepin (**5**),<sup>18</sup> respectively. Especially, the <sup>1</sup>H NMR spectra of both **4** and **5** reveal similar symmetrical patterns with only 3 singlet signals assignable to the methyl groups of the bornane skeletons, ie, 0.80 ppm (6 H, s), 0.81 ppm (6 H, s), and 1.00 ppm (6 H, s) for compound **4**, and 0.82 ppm (6 H, s), 0.87 ppm (6 H, s), and 1.05 ppm (6 H, s) for compound **5**, despite the difference in their parent ion peaks in the mass spectra, ie, *m/z* 428 (M<sup>+</sup>) for **4** and *m/z* 507 (M<sup>+</sup>) for **5**, respectively. Furthermore, physical and spectral data of compound **5** were identical with those of 1,2,5-triselenepin **5** reported previously by us.<sup>18</sup>

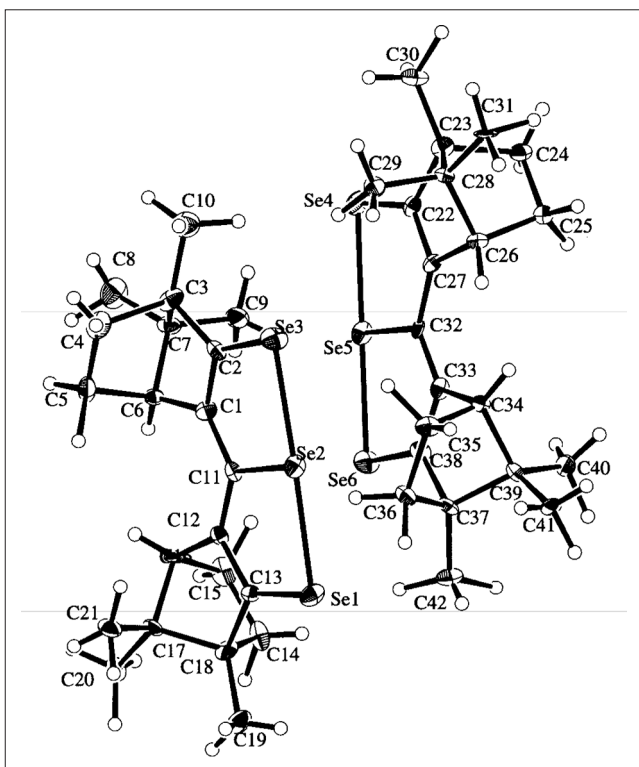
The other three compounds were also subjected to chromatographic separation, and all physical and spectral data for these compounds involving MS, IR, <sup>1</sup>H NMR, <sup>13</sup>C NMR, and elemental analysis were also fully assignable to symmetrical 1,6,6 $\alpha$ ^4-triselenapentalene (**6**) (purple crystals), symmetrical 4*H*-selenopyran-4-selone (**7**) (green crystals), and unsymmetrical 4*H*-selenopyran-4-selone (**8**) (green crystals). The <sup>1</sup>H NMR spectra of both **6** and **7** revealed similar symmetrical spectral patterns with only 3 methyl signals of two bornane skeletons, ie 0.68 ppm (6 H, s), 0.99 ppm (6 H, s), and 1.32 ppm (6 H, s) for **6**, and 0.75 ppm (6 H, s), 0.96 ppm (6 H, s), and 1.28 ppm (6 H, s) for **7**. Especially, the <sup>77</sup>Se NMR spectrum of **6** revealed a characteristic symmetrical Se-Se-Se patterns of 572.3 ppm (d, *J*<sub>Se-Se</sub> = 294 Hz) and 1079.5 ppm (*t*, *J*<sub>Se-Se</sub> = 294 Hz) attributed



**Figure 2.** An ORTEP drawing of 1,2,5-triselenepin **5**.

to the  $1,6,6\alpha\lambda^4$ -triselenapentalene core. On the other hand, the  $^1\text{H}$  NMR spectral pattern of compound **8** revealed an unsymmetrical spectral pattern with 6 methyl signals, ie, 0.74 ppm (3 H, s), 0.75 ppm (3 H, s), 0.94 ppm (3 H, s), 0.95 ppm (3 H, s), 1.26 ppm (3 H, s), and 1.74 ppm (3 H, s). It is worth noting that both **7** and **8** are green crystalline compounds with weak absorption peaks assignable to the  $n-\pi^*$  transition of the selenocarbonyl functionality at 619 nm ( $\epsilon = 370$ ) for **7** and 723 nm ( $\epsilon = 380$ ) for **8**, respectively, in the visible light region.

The structures of these compounds were finally determined by X-ray crystallographic analyses to be symmetrical 1,2,5-triselenepin **5**,  $1,6,6\alpha\lambda^4$ -triselenapentalene **6**, and unsymmetrical 4*H*-selenopyran-4-selone **8**, and their Oak Ridge Thermal-Ellipsoid Plot Program (ORTEP) drawings of **5**, **6**, and **8** are depicted in Figures 2–4, respectively. On the other

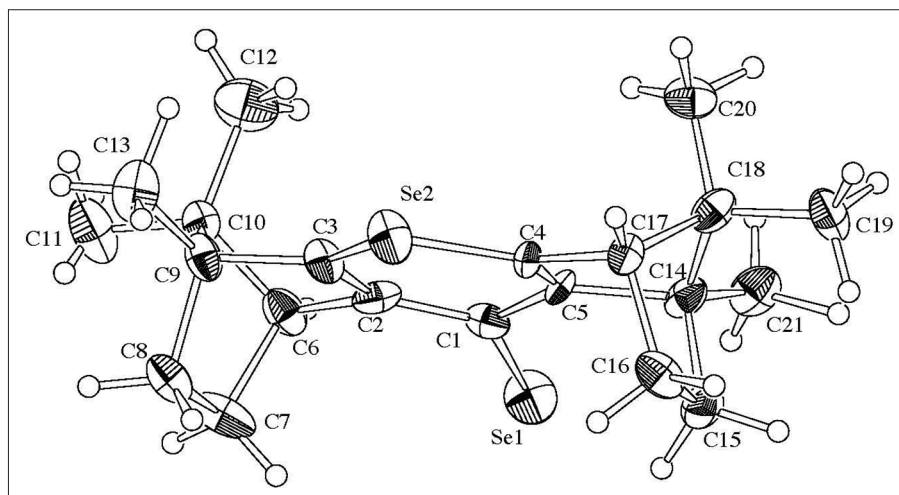


**Figure 3.** An ORTEP drawing of  $1,6,6\alpha\lambda^4$ -triselenapentalene (**6**).

hand, the X-ray analysis of **4** and **7** was not successful. However, 1,2,5-triselenepin **5** was gradually converted into compound **4** along with selenium extrusion by doping **5** in silica gel at room temperature for a long time as shown in Scheme 2, and these results strongly suggest the structure of compound **4** to be symmetrical 1,4-diselenin. Therefore, the alternative possible structures, such as 1,2-diselenin **4'**<sup>61,62</sup> formed through [3,3] sigmatropic rearrangement of dialkenyl diselenide **2** and the isomeric unsymmetrical 1,4-diselenin **4''**, are excluded.

According to the result of X-ray crystal data of **6**, the  $1,6,6\alpha\lambda^4$ -triselenapentalene ring system of **6** possesses a planar and symmetrical structure with a linear arrangement of Se(1)-Se(2)-Se(3) atoms and almost parallel 3 carbon–selenium bonds with the right Se-Se-C bond angles, ie,  $88.2^\circ$  for Se(1)-Se(2)-C(11),  $88.8^\circ$  for Se(3)-Se(2)-C(11),  $87.0^\circ$  for Se(2)-Se(3)-C(2), and  $87.2^\circ$  for Se(2)-Se(1)-C(13), respectively. Furthermore, the bond lengths of Se(1)-Se(2) and Se(2)-Se(3) were equal and the bond lengths of the central hypervalent Se(2) and the C(11) atom were also similar to those of Se(1)-C(13) and Se(3)-C(2) bonds, ie, 1.82 Å for Se(1)-C(13), 1.92 Å for Se(2)-C(11), and 1.84 Å for Se(3)-C(2), respectively. In addition, the bond lengths of C(2)-C(1), C(1)-C(11), C(11)-C(12), and C(12)-C(13) were almost equal each other. These X-ray data indicated that the  $1,6,6\alpha\lambda^4$ -triselenapentalene ring system possesses the heteroaromaticity. Therefore, the high field shift of 1 singlet signal of the methyl group ( $\delta = 0.68$  ppm) in the  $^1\text{H}$  NMR spectrum of **6** was explained by the anisotropic effect of the  $1,6,6\alpha\lambda^4$ -triselenapentalene ring, and the existence of the 3  $\text{sp}^2$  carbon signals ( $\delta = 152.9$ , 169.2, and 195.2 ppm) in the  $^{13}\text{C}$  NMR spectrum of **6** was also explained by the central  $\text{sp}^2$  carbon atom (=C(11)) of the heterocyclic ring of **6**. The  $^{77}\text{Se}$  NMR spectrum of **6** also revealed 2 selenium signals ( $\delta = 573.2$  and 1079.5 ppm) with a symmetrical Se-Se-Se coupling pattern, and the evidences for bond switching between the Se(1)-Se(2) and the Se(2)-Se(3) bonds of **6** through a tautomeric equilibration between **6'** and **6''** as shown in Scheme 3 were not observed from these NMR spectra. All the results suggest the heteroaromatic stabilization of  $1,6,6\alpha\lambda^4$ -triselenapentalene ring of **6**.

In contrast, the heterocyclic ring system of **8** was confirmed to be an unexpected 4*H*-selenopyran-4-selone ring with unsymmetrically fused two bornane skeletons. Especially, the bond lengths of C(1)=Se(1) were almost equal to those of C(3)-Se(2) and C(4)-Se(2) of the core heterocyclic ring system, ie, 1.839 Å for C(1)=Se(1), 1.846 Å for C(3)-Se(2), and 1.81 Å for C(4)-Se(2), respectively, and the bond lengths of the carbon–carbon bonds of the ring system were also much similar to each other, ie, 1.39 Å for C(1)-C(2), 1.42 Å for C(1)-C(5), 1.37 Å for C(2)=C(3), and 1.39 Å for C(4)=C(5), respectively. In addition, the 4*H*-selenopyran ring was almost planar with small torsion angles of the 4 atoms of the ring, ie,  $-1^\circ$  for Se(2)-C(3)-C(2)-C(1),  $7^\circ$  for C(2)-C(3)-Se(2)-C(4),  $-1^\circ$  for C(3)-Se(2)-C(4)-C(5), and  $11^\circ$  for Se(2)-C(4)-C(5)-C(1), respectively. These results strongly suggested that the

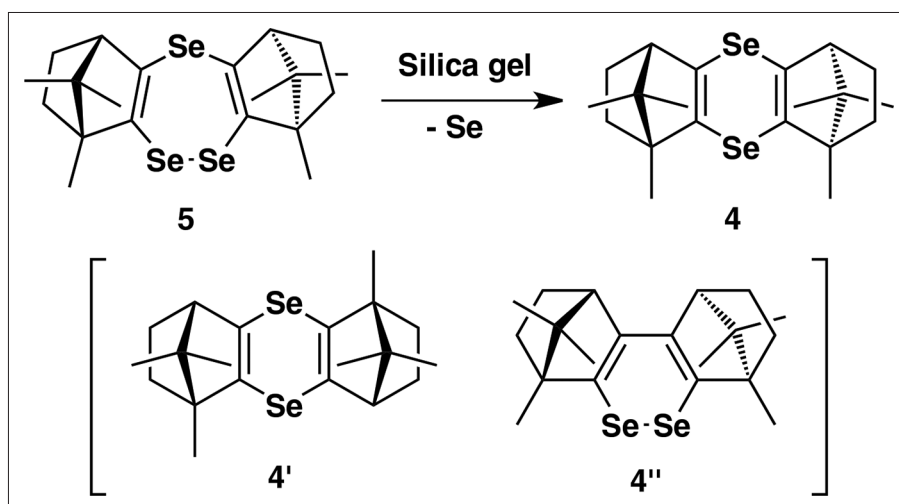


**Figure 4.** An ORTEP drawing of 4*H*-selenopyran-4-selone (**8**).

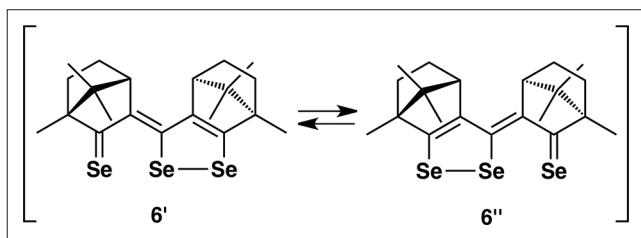
4*H*-selenopyran-4-selone ring of **8** has a contribution of the tautomeric structure of heteroaromatic selenopyrylium ion **8'** as shown in Scheme 4.

Selones **7** and **8** were unstable toward exposure to air and underwent gradual decomposition to afford the corresponding ketones quantitatively along with extrusion of elemental selenium. All physical and spectral data for these products involving MS, IR,  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, and elemental analysis were fully consistent to symmetrical and unsymmetrical 4*H*-selenopyran-4-ones **9** and **10**, respectively.<sup>63,64</sup> In contrast, compound **6** was stable enough toward the exposure to air, sunlight, heating, and sodium borohydride ( $\text{NaBH}_4$ ) reduction. The stability of **6** toward such reagents might also be explained by the heteroaromatic character of the 1,6,6a $\lambda^4$ -trisenapentalene ring system. However, when a  $\text{CHCl}_3$  solution of **6** was treated with *m*-chloroperbenzoic acid (*m*CPBA, 3.0 mol amt.) at room temperature for 0.5 hours, 1,2-diselenole

(**11**) was obtained in 81% yield along with 4*H*-selenopyran-4-one (**9**) (trace) and some uncharacterized products (trace) along with the recovery of **6** (6%) as shown in Scheme 5. Therefore, the structure of selone **7** was confirmed to be a 4*H*-selenopyran-4-selone with symmetrically fused two bornane skeletons. The mass spectrum of **11** revealed the parent ion peak at  $m/e$  456 as the base peak, and the IR spectrum of **11** reveals a strong C = O stretching band at  $1714\text{ cm}^{-1}$ . The carbonyl carbon signal was also observed at  $\delta = 204.5\text{ ppm}$  in its  $^{13}\text{C}$  NMR spectrum, and all other physical and spectral data involving the  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, and elemental analysis data were fully consistent to the structure of **11** bearing a carbonyl group at the C-2 position of one bornane skeleton. Especially, the  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra of **11** revealed the unsymmetrical patterns, and the structure of symmetrical cyclic diselenide **11'** was excluded. It was assumed that the unusual selenium-oxygen replacement of 1,6,6a $\lambda^4$ -trisenapentalene ring forming 1,2-diselenole ring



**Scheme 2.** Conversion of symmetrical 1,2,5-triselenepin (**5**) into 1,4-diselenin (**4**).



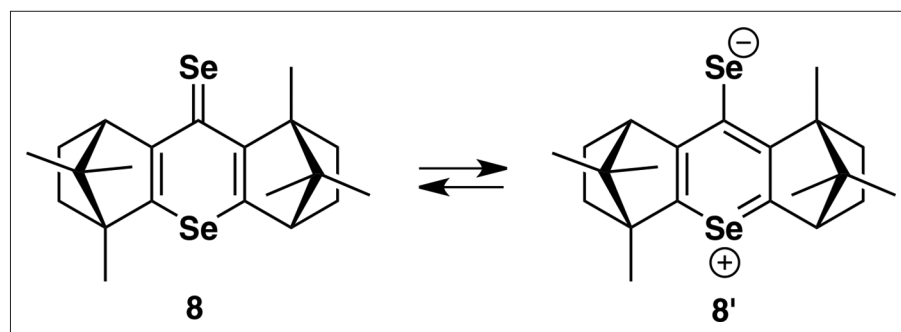
**Scheme 3.** Possible bond-switching tautomerization for compound **6**.

and a carbonyl group would proceed through oxidation of an electron-rich selenium atom, Se(1) or Se(3) of **6**, via the plausible bond-switching tautomerization between **6'** and **6''**.<sup>38-50</sup> In addition, the structure of **11**, bearing an isolated carbonyl group, strongly suggested that the formation of 1,6,6 $\alpha$ <sup>4</sup>-oxadiselenapentalene ring would be unfavorable due to the weak attractive interaction between the selenium atoms of the 1,2-diselenole ring and the oxygen atom of the neighboring carbonyl group.

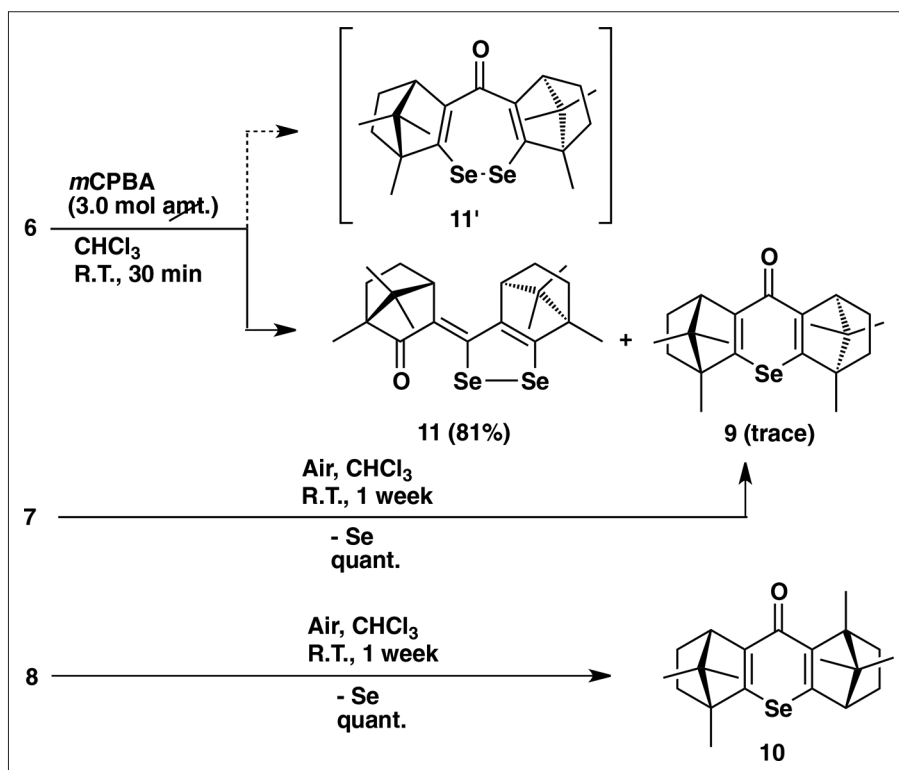
In contrast to the case of *d*-camphor *p*-toluenesulfonylhydrazone (**1**), similar treatment of cyclopentanone *p*-toluenesulfonylhydrazone with *t*-BuOK and elemental selenium at 110°C for 3 hours only afforded the corresponding dialkenyl diselenide in 35% yield along with the formation of a complex mixture of uncharacterized products, and neither 1,6,6 $\alpha$ <sup>4</sup>-triselenapentalene nor 4*H*-selenopyen-4-selones was found at all in the mixture. This result strongly suggested that the steric protection by the bulky bornane substituents was much effective for the stabilization of selenium-containing products **5-8**. However, attempts for trapping of the precursors of **6-8** by applying various trapping agents were not successful at all even in the case starting from *d*-camphor *p*-toluenesulfonylhydrazone (**1**).

The reaction pathway for the formation of products **4-8** remains unclear. However, dibornenyl diselenide **2** was mainly obtained and **4-8** were not found at all in the crude product when the reaction of **1** with *t*-BuOK and elemental selenium at 140°C for 3 hours, and the prolong reaction time for the same reaction, in turn, afforded **4-8** along with lowering of the yield

of **2** as presented in Table 1. These experimental results suggested that **4-8** are just the secondary products formed from borneneselenolate ion **B** and the alternative pathway via 1,2,3-selenadiazole and/or selenirene intermediates from **1** would be negligible. Therefore, it is assumed that the products **4** and **5** would be afforded through a plausible pathway involving the *in situ* generation of  $\beta$ -selenoxoselenolate ion **G** formed through the reaction of borneneselenolate ion **B** with elemental selenium, the subsequent formation of unstable cyclic polyselenides **H**, and the final thermal or oxidative selenium extrusion to result in the formation of relatively stable symmetrical 1,4-diselenins **4** and symmetrical 1,2,5-triselenepins **5**. Though we could not isolate their isomeric products, **4'** and **5'**, these compounds would also be formed as the minor components through this pathway and would be contained in the uncharacterized mixture of selenium-containing products. 1,3,5-Trithiones are generally recognized as the synthetic precursors of 1,6,6 $\alpha$ <sup>4</sup>-trithiapentalenes.<sup>38-50</sup> Therefore, it was assumed that the precursor of 1,6,6 $\alpha$ <sup>4</sup>-triselenapentalene **6** should be 1,3,5-triselenone or its alkeneselenolate-type intermediates **J** formed through homologation of borneneselenolate ion **B** at the C-3 position. Actually, treatment of compound **1** with *t*-BuOK and elemental selenium in HMPA afforded only **2**, **3**, and **5**, and neither **6**, **7**, nor **8** were found at all in the crude products as shown in Table 1. This result strongly suggests that DMF, used as the solvent of the reactions, behaves as the C<sub>1</sub> source for the formation of **6-8**. Formation of selenocarbamate ions (**I**) by treating DMF with a base and elemental selenium has been reported previously,<sup>15,65-69</sup> and, therefore, it was assumed that formylation or selenoformylation at the C-3 position of the bornane skeleton<sup>70,71</sup> would proceed through the reaction of alkeneselenolate ion **B** with selenocarbamate ion (**I**) or its related derivatives under the strong basic conditions to form 1,3,5-triselenoxo-type intermediate **J**<sup>72</sup> as shown in Scheme 6. However, addition of C<sub>1</sub> sources, such as potassium carbonate (K<sub>2</sub>CO<sub>3</sub>), dimethyl carbonate, or CHCl<sub>3</sub> in the reaction mixture did not affect the results at all, and introduction of CO<sub>2</sub> gas to the reaction atmosphere only showed a slight improvement on the combined yield of **6-8**. All the results of the attempts for optimization of the reaction condition are summarized in Table 1. The formation mechanism of



**Scheme 4.** Structures of 4*H*-selenopyran-4-selone (**8**) and its tautomeric selenopyrylium ion (**8'**).



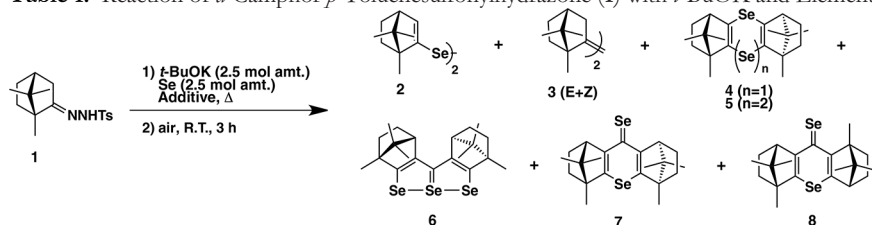
**Scheme 5.** Oxidation of 1,6,6 $\alpha$  $\lambda$ <sup>4</sup>-triselenapentalene (6) and 4*H*-selenopyran-4-selones (7, 8).

unsymmetrical 4*H*-selenopyran-4-selone **8** also remained unclear at this time, but **8** was obtained as the minor component in all cases in contrast to **7**, and **8** was assumed to be formed through a different pathway involving the reaction of

2-bornene or its carbene-type precursor generated in situ through Bamford–Stevens reaction of substrate **1**.<sup>73</sup>

In conclusion, we found a new method for the synthesis of 1,6,6 $\alpha$  $\lambda$ <sup>4</sup>-triselenapentalene (**6**) and 4*H*-selenopyran-4-selones

**Table 1.** Reaction of *d*-Camphor *p*-Toluenesulfonylhydrazone (**1**) with *t*-BuOK and Elemental Selenium.



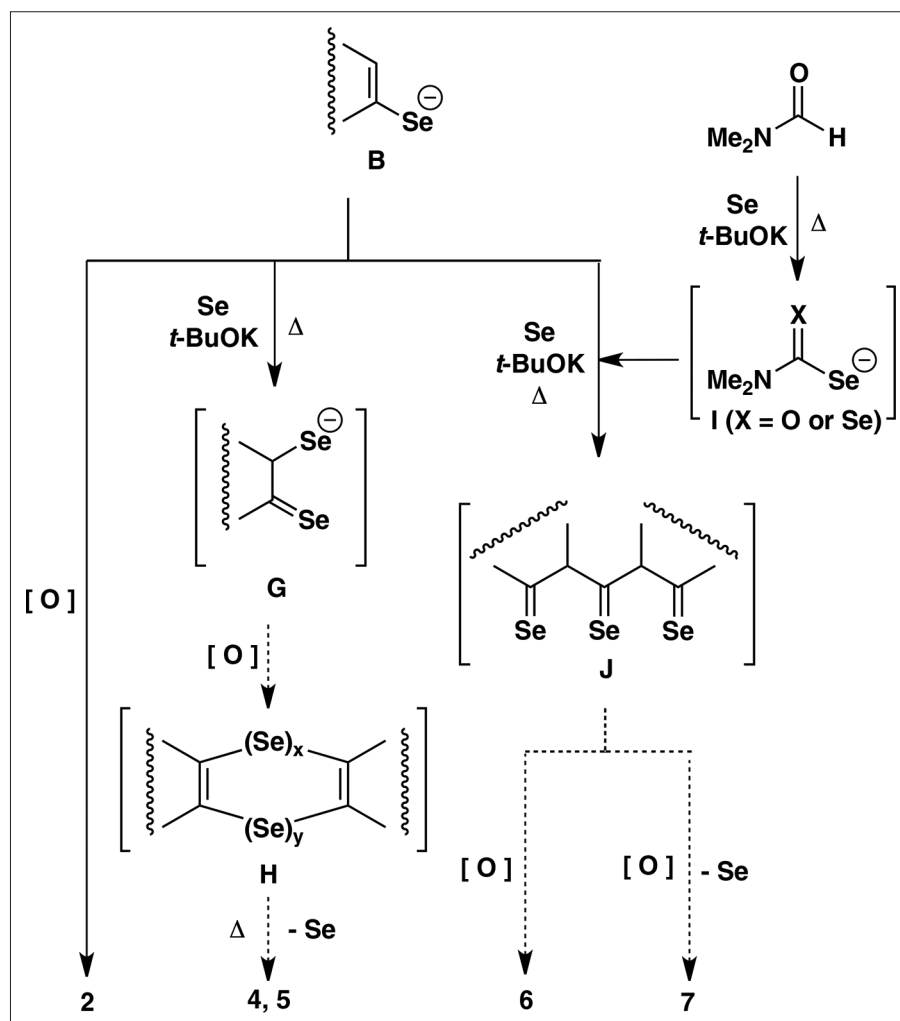
Solvent	Additive (mol amt.)	Atmosphere	Temp (°C)	Time (h)	Yield (%) <sup>a</sup>						
					<b>2</b>	<b>3</b> <sup>b</sup>	<b>4</b>	<b>5</b> <sup>b</sup>	<b>6</b>	<b>7</b>	<b>8</b>
HMPA	-	Ar	120	3	64	30	0	5	0	0	0
DMF	-	Ar	140	3	46	18	0	0	2	4	1
DMF	-	Ar	140	24	10	15	17	15	5	3	Trace
DMF	-	Ar $\rightarrow$ CO <sub>2</sub> <sup>c</sup>	140	2	40	20	0	0	5	6	2
DMF	K <sub>2</sub> CO <sub>3</sub> (2.5)	Ar	140	24	7	32	0	0	6	2	1

DMF, dimethylformamide; HMPA, hexamethylphosphoric triamide.

<sup>a</sup>Isolated yields.

<sup>b</sup>About 3:2 mixture of *E*- and *Z*-olefins **3**.

<sup>c</sup>A DMF solution of **1** was treated with *t*-BuOK and elemental selenium under an argon atmosphere and then dry CO<sub>2</sub> gas was introduced to the reaction atmosphere along with an additional heating for 1.5 hours.



**Scheme 6.** Plausible pathway for the formation of 4-7.

(7 and 8). Especially, our new findings on the short-step preparation of sterically crowded 1,6,6 $\alpha$  $\lambda^4$ -triselenapentalene (**6**) are recognized to be synthetically useful by providing us a new motif of potential redox-permeable selenium compounds for the practical uses such as the components of organic electronic devices, and further studies on the reactivity of selenurane **6** involving their redox behaviors are expected in our laboratory.

## Experimental

### Instruments

The melting points were determined with a Büchi 535 micro melting point apparatus.  $^1\text{H}$  NMR spectra were recorded on a Bruker AC-400P (400 MHz) spectrometer, and the chemical shifts of the  $^1\text{H}$  NMR spectra are given in  $\delta$  relative to internal tetramethylsilane.  $^{13}\text{C}$  NMR spectra were recorded on a Bruker AC-400P (100 MHz).  $^{77}\text{Se}$  NMR spectra were recorded on a Bruker AC-400P (76 MHz). Mass spectra were recorded on a Hitachi M-2000 mass spectrometer with electron-impact

ionization at 20 or 70 eV using a direct inlet system. IR spectra were recorded for thin film (neat) or KBr disks on a JASCO FT/IR-7300 spectrometer. Elemental analyses were performed using a Yanagimoto CHN corder MT-5.

### Materials

Column chromatography was performed using silica gel (Merck, Cat. No. 7734 or 9385) without pretreatment. Dichloromethane and chloroform were dried over phosphorus pentoxide and were freshly distilled before use. *N,N*-DMF and HMPA were dried over calcium hydride and were freshly distilled before use. Ethanol was dried over magnesium oxide and was freshly distilled before use. All substrates and reagents including cyclopentanone, *d*-camphor, *p*-toluenesulfonylhydrazide, acetic acid, potassium *t*-BuOK, elemental sulfur, elemental selenium, anhydrous potassium carbonate ( $\text{K}_2\text{CO}_3$ ), anhydrous sodium sulfate ( $\text{Na}_2\text{SO}_4$ ), sodium thiosulfate ( $\text{Na}_2\text{S}_2\text{O}_3$ ),  $\text{NaBH}_4$ , and *m*CPBA were

commercially available reagent grade and were used without any pretreatment.

*General Procedure for the Reaction of Ketone p-Toluenesulfonylhydrazones with Potassium t-Butoxide and Elemental Selenium.* A 30 mL DMF solution of *p*-toluenesulfonylhydrazone **1** (5.00 mmol) was treated with elemental selenium (1.00 g, 12.5 mmol) and potassium *t*-butoxide (1.40 g, 12.5 mmol) at room temperature, and the reaction mixture was heated at 100°C-150°C under an argon atmosphere for several hours. The reaction was then cooled to room temperature and was exposed to air for a few hours. The reaction was quenched with water and extracted with benzene. The organic layer was washed with water and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> powder. After removing the solvent *in vacuo*, the crude product was purified using column chromatography on silica gel to afford dialkenyl diselenide **2**, *E/Z* mixture of dimeric olefins **3**, and several minor components (**4**, **5**, **6**, **7**, and **8**).

### Physical and Spectral Data for Dialkenyl Diselenide **2**<sup>18</sup>

**2**: Orange oil.

IR (neat): 2951, 2870, 1449, 1385, 1155 cm<sup>-1</sup>.

<sup>1</sup>H NMR (CDCl<sub>3</sub>) δ: 0.81 (6H, s), 0.85 (6H, s), 1.08 (6H, s), 1.21-1.82 (8H, m), 2.33-2.40 (2 H, m), 5.73 (2H, d, *J* = 2.1 Hz).

<sup>13</sup>C NMR (CDCl<sub>3</sub>) δ: 12.9 (q), 18.9 (q), 19.1 (q), 25.5 (t), 31.3 (t), 54.5 (d), 60.3 (s), 62.2 (s), 129.7 (d) 137.4 (s).

MS (*m/z*): 430 (M<sup>+</sup>; 4%, <sup>80</sup>Se), 215 (M<sup>+</sup>/2; 7%, <sup>80</sup>Se), 41 (bp).

Calcd for C<sub>20</sub>H<sub>30</sub>Se<sub>2</sub>: C, 56.08; H, 7.06%. Found: C, 55.93; H, 7.03%.

### Mixture of Dimeric *E*- and *Z*-Olefins **3** (Approximately 3:2 Mixture)<sup>18,59,60</sup>

Colorless oil.

MS (*m/z*): 272 (M<sup>+</sup>; bp).

IR (KBr): 2951, 2866, 1468, 1448, 1386, 1372, 1365 cm<sup>-1</sup>.

Calcd for C<sub>20</sub>H<sub>32</sub>: C, 88.16; H, 11.84%. Found: C, 87.46; H, 11.10%.

### Plausible *E*-Isomer **3**

<sup>1</sup>H NMR (CDCl<sub>3</sub>) δ: 0.78 (12H, s), 1.01 (6H, s).

<sup>13</sup>C NMR (CDCl<sub>3</sub>) δ: 14.6 (q), 18.6 (q), 19.8 (q), 27.8 (t), 34.0 (t), 37.1 (t), 44.7 (s), 47.4 (s), 52.4 (s), 135.5 (s).

### Plausible *Z*-Isomer **3**

<sup>1</sup>H NMR (CDCl<sub>3</sub>) δ: 0.70 (6H, s), 0.78 (6H, s), 1.09 (6H, s).

<sup>13</sup>C NMR (CDCl<sub>3</sub>) δ: 17.0 (q), 19.6 (q), 20.5 (q), 28.5 (t), 35.7 (t), 40.1 (t), 43.8 (s), 50.6 (d), 137.7 (s).

### Physical and Spectral Data for 1,4-Diselenin **4**

Pale yellow needles.

MP: 122.0°C-123.0°C

IR (KBr): 2987, 1544, 1386, 1111, 817 cm<sup>-1</sup>.

<sup>1</sup>H NMR (CDCl<sub>3</sub>) δ: 0.80 (6H, s), 0.81 (6H, s), 1.00 (6H, s), 1.55-1.60 (4H, m), 1.79-1.85 (4 H, m), 2.31 (2H, d, *J* = 3.6 Hz).

<sup>13</sup>C NMR (CDCl<sub>3</sub>) δ: 12.5 (q), 19.1 (q), 19.5 (q), 25.6 (t), 32.5 (t), 57.3 (s), 57.9 (d), 58.6 (s), 128.5 (s), 133.4 (s).

MS (*m/z*): 428 (M<sup>+</sup>; bp, <sup>80</sup>Se), 214 (M<sup>+</sup>/2; 12%, <sup>80</sup>Se).

Calcd for C<sub>20</sub>H<sub>28</sub>Se<sub>2</sub>: C, 56.34; H, 6.62%. Found: C, 56.18; H, 6.77%.

### Physical and Spectral Data for 1,2,5-Triselenepin **5**<sup>18</sup>

Orange solids.

MP: 162.0°C-163.0°C

[α]<sub>D</sub><sup>20</sup> = -191.3° (*c* 0.1, CHCl<sub>3</sub>).

IR (KBr): 2952, 1528, 1386, 1107, 813 cm<sup>-1</sup>.

<sup>1</sup>H NMR (CDCl<sub>3</sub>) δ: 0.82 (6H, s), 0.87 (6H, s), 1.05 (6H, s), 1.12-1.30 (4H, m), 1.51-1.59 (2 H, m), 1.78-1.85 (2H, m), 2.38 (2H, d, *J* = 3.7 Hz).

<sup>13</sup>C NMR (CDCl<sub>3</sub>) δ: 12.9 (q), 18.9 (q), 191. (q), 25.6 (dd), 31.3 (t), 54.4 (s), 60.3 (d), 62.2 (s), 137.3 (s), 145.2 (s).

<sup>77</sup>Se NMR (CDCl<sub>3</sub>) δ: 357.0, 527.2.

MS (*m/z*): 508 (M<sup>+</sup>; 17%, <sup>80</sup>Se), 105 (bp).

Calcd for C<sub>20</sub>H<sub>28</sub>Se<sub>3</sub>: C, 47.54; H, 5.59%. Found: C, 47.30; H, 5.59%.

*X-Ray Crystallographic Data for 5.* Colorless prism, monoclinic, P2<sub>1</sub> (#4), *a* = 7.857(3) Å, *b* = 14.637(5) Å, *c* = 9.005(4) Å, β = 97.09(3)°, *V* = 1027.7(6) Å<sup>3</sup>, *Z* = 2, *D*<sub>calc</sub> = 1.633 g/cm<sup>3</sup>, μ(MoKα) = 53.68 cm<sup>-1</sup>, *R* = 0.025, *R*<sub>w</sub> = 0.026. The data were deposited in Crystallographic Data Center (CCDC-1954439).

Selected bond lengths (Å), bond angles (deg), and torsion angles (deg) of compound **5**: Se(1)-C(1), 1.894(5); Se(1)-C(8), 1.880(5); Se(2)-Se(3), 2.3452(8); Se(2)-C(2), 1.892(4); Se(3)-C(9), 1.887(5); C(1)-C(2), 1.337(7); C(8)-C(9), 1.351(7); C(1)-Se(1)-C(8), 113.0(2); Se(3)-Se(2)-C(2), 100.0(2); Se(2)-Se(3)-C(9), 100.3(1); Se(1)-C(1)-C(2), 138.1(4); Se(1)-C(1)-C(5), 114.4(3); C(2)-C(1)-C(5), 107.2(4); Se(2)-C(2)-C(1), 127.9(4); Se(2)-C(2)-C(3), 123.9(3); C(1)-C(2)-C(3), 107.5(4); Se(1)-C(8)-C(9), 136.0(4); Se(1)-C(8)-C(12), 116.5(3); C(9)-C(8)-C(12), 106.9(4); Se(3)-C(9)-C(8), 128.2(4); Se(3)-C(9)-C(10), 123.3(4); C(8)-C(9)-C(10), 107.6(4); Se(1)-C(1)-C(2)-Se(2), -1.3(9); Se(1)-C(1)-C(2)-C(3), -171.8(5); Se(1)-C(1)-C(5)-C(4), -151.6(4); Se(1)-C(1)-C(5)-C(6), 102.2(4); Se(1)-C(8)-C(9)-Se(3), 0.0(9); Se(1)-C(8)-C(9)-C(10), -169.8(5); Se(1)-C(8)-C(12)-C(11), -153.5(4); Se(1)-C(8)-C(12)-C(13), 100.1(4); Se(2)-Se(3)-C(9)-C(8), -57.3(5); Se(2)-Se(3)-C(9)-C(10), 111.0(4); Se(2)-C(2)-C(1)-C(5), 171.9(4); Se(2)-C(2)-C(3)-C(4), 154.0(4); Se(2)-C(2)-C(3)-C(7), -100.6(5); Se(2)-C(3)-C(17), 26.6(7); Se(3)-Se(2)-C(2)-C(1), -53.9(5); Se(3)-Se(2)-C(2)-C(3), 115.3(5); Se(3)-C(9)-C(8)-C(12), 170.8(4); Se(3)-C(9)-C(10)-C(11), 155.6(3); Se(3)-C(9)-C(10)-C(14), -100.2(4); Se(3)-C(9)-C(10)-C(20), 26.9(7); C(1)-Se(1)-C(8)-C(9), 19.8(7); C(1)-Se(1)-C(8)-C(12), -150.3(4); C(1)-C(2)-C(3)-C(4), -34.9(6); C(1)-C(2)-C(3)-C(7),



70.4(5); C(1)-C(2)-C(3 - 17), -162.3(5); C(2)-Se(2)-Se(3)-C(9), 81.8(2); C(2)-C(1)-Se(1)-C(8), 16.9(7); C(2)-C(1)-C(5)-C(4), 33.3(6); C(2)-C(1)-C(5)-C(6), -72.9(5); C(5)-C(1)-Se(1)-C(8), -156.0(4); C(8)-C(9)-C(10)-C(11), -34.1(5); C(8)-C(9)-C(10)-C(14), 70.2(5).

### Physical and Spectral Data for 1,6,6a $\lambda^4$ -Triselenapentalene 6

Dark red needles.

MP: 173.0°C-176.0°C

$[\alpha]_D^{20} = +280.0^\circ$  ( $c$  0.1, CHCl<sub>3</sub>).

UV (C<sub>2</sub>H<sub>5</sub>OH)  $\lambda_{\max}$ : 287 nm ( $\epsilon = 37100$ ), 536 nm ( $\epsilon = 3460$ ), 596 nm ( $\epsilon = 2100$ ).

IR (KBr): 2953, 2922, 2867, 1435, 1283, 1104 cm<sup>-1</sup>.

<sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ : 0.68 (6H, s), 0.99 (6H, s), 1.26-1.34 (4H, m), 1.32 (6H, s), 1.69-1.75 (2H, m), 2.17-2.24 (2 H, m), 3.43 (2H, d,  $J = 3.8$  Hz).

<sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$ : 13.7 (q), 19.8 (q), 20.3 (q), 26.1 (dd), 29.7 (t), 32.0 (dd), 55.7 (d), 57.7 (s), 61.9 (s), 152.9 (s), 169.2 (s), 195.1 (s).

<sup>77</sup>Se NMR (CDCl<sub>3</sub>)  $\delta$ : 572.3 (d,  $J_{\text{Se-Se}} = 294$  Hz), 1079.5 (t,  $J_{\text{Se-Se}} = 294$  Hz).

MS ( $m/z$ ): 520 (M<sup>+</sup>; 10%, <sup>80</sup>Se), 290 (bp).

Calcd for C<sub>21</sub>H<sub>28</sub>Se<sub>3</sub>: C, 48.76; H, 5.46%. Found: C, 48.89; H, 5.48%.

*X-Ray Crystallographic Data for 6.* Red needle, monoclinic, P2<sub>1</sub> (#4),  $a = 15.668(1)$  Å,  $b = 8.3478(8)$  Å,  $c = 16.072(3)$  Å,  $\beta = 96.371(3)^\circ$ ,  $V = 2089.0(4)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_{\text{calc}} = 1.607$  g/cm<sup>3</sup>,  $\mu(\text{MoK}\alpha) = 52.84$  cm<sup>-1</sup>,  $R = 0.045$ ,  $R_w = 0.049$ . The data were deposited in Cambridge Crystallographic Data Center (CCDC-1954440).

Selected bond lengths (Å), bond angles (deg), and torsion angles (deg) of compound **6**: Se(1)-Se(2), 2.590(2); Se(2)-Se(3), 2.585(2); Se(1)-C(13), 1.82(1); Se(2)-C(11), 1.928(10); Se(3)-C(2), 1.84(1); C(1)-C(2), 1.36(1); C(1)-C(11), 1.40(1); C(11)-C(12), 1.40(1); C(12)-C(13), 1.38(1); Se(2)-Se(1)-C(13), 87.2(3); Se(1)-Se(2)-C(11), 88.2(3); Se(2)-Se(3)-C(2), 87.0(3); Se(1)-Se(2)-Se(3), 176.98(7); Se(3)-Se(2)-C(11), 88.8(3); Se(3)-C(2)-C(3), 127.5(8); Se(2)-C(11)-C(12), 117.1(7); Se(1)-C(13)-C(12), 123.8(7); Se(2)-C(11)-C(1), 116.0(7); Se(1)-Se(2)-Se(3)-C(2), 9(1); Se(1)-Se(2)-C(11)-C(1), -177.3(7); Se(1)-Se(2)-C(11)-C(12), 3.6(7); Se(1)-C(13)-C(12)-C(11), 2(1); Se(1)-C(13)-C(12)-C(16), 178.1(7); Se(1)-C(13)-C(18)-C(14), -107(1); Se(1)-C(13)-C(18)-C(17), 148.3(8); Se(1)-C(13)-C(18)-C(19), 19(1); Se(2)-Se(1)-C(13)-C(12), 1.0(8); Se(2)-Se(1)-C(13)-C(18), 176.6(9); Se(2)-Se(3)-C(2)-C(1), -2.1(8); Se(2)-Se(3)-C(2)-C(3), 172.5(9); Se(2)-C(11)-C(1)-C(2), -5(1); Se(2)-C(11)-C(1)-C(6), -177.0(8); Se(2)-C(11)-C(12)-C(13), -4(1); Se(2)-C(11)-C(12)-C(16), -179.8(7); Se(3)-Se(2)-Se(1)-C(13), -12(1); Se(3)-Se(2)-C(11)-C(1), 2.2(7); Se(3)-Se(2)-C(11)-C(12), -176.9(7); Se(3)-C(2)-C(1)-C(6), 178.6(7); Se(3)-C(2)-C(1)-C(11), 5(1); Se(3)-C(2)-C(3)-C(4), -108(1); Se(3)-C(2)-C(3)-C(7), 150.3(8); Se(3)-C(2)-C(3)-C(10), 20(1);

C(2)-Se(3)-Se(2)-C(11), -0.2(4); C(11)-Se(2)-Se(1)-C(13), -2.2(4).

### Physical and Spectral Data for Symmetrical 4H-Selenopyran-4-Selone 7

Green needles.

MP: 180.7°C-181.4°C (dec.).

$[\alpha]_D^{20} = +108^\circ$  ( $c$  0.01, CHCl<sub>3</sub>).

UV (C<sub>2</sub>H<sub>5</sub>OH)  $\lambda_{\max}$ : 207 nm ( $\epsilon = 23700$ ), 234 nm ( $\epsilon = 17550$ ), 319 nm ( $\epsilon = 17980$ ), 456 nm ( $\epsilon = 33210$ ), 619 nm ( $\epsilon = 370$ ).

MS ( $m/z$ ): 440 (M<sup>+</sup>; bp, <sup>80</sup>Se), 425 (M<sup>+</sup>-CH<sub>3</sub>; 41%, <sup>80</sup>Se), 410 (M<sup>+</sup>-2CH<sub>3</sub>; 30%, <sup>80</sup>Se).

IR (KBr): 2938, 2868, 1518, 1467, 1442, 1380, 1229, 1142, 1065, 739 cm<sup>-1</sup>.

<sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ : 0.75 (6H, s), 0.96 (6H, s), 1.28 (6H, s), 1.77-1.84 (4H, m), 2.06-2.13 (4 H, m), 3.89 (2H, d,  $J = 3.8$  Hz).

<sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$ : 12.4 (q), 19.1 (q), 19.3 (q), 24.2 (dd), 33.2 (dd), 56.1 (s), 57.4 (d), 60.8 (s), 153.1 (s), 158.4 (s), 188.4 (s).

Calcd for C<sub>21</sub>H<sub>28</sub>Se<sub>2</sub>: C, 57.54; H, 6.44%. Found: C, 57.10; H, 6.23%.

### Physical and Spectral Data for Unsymmetrical 4H-Selenopyran-4-Selone 8

Metallic green plates.

MP: 170.5°C-172.2°C (dec.).

$[\alpha]_D^{20} = +297^\circ$  ( $c$  0.01, CHCl<sub>3</sub>).

UV (hexane)  $\lambda_{\max}$ : 210 nm ( $\epsilon = 25760$ ), 274 nm ( $\epsilon = 3130$ ), 313 nm ( $\epsilon = 14450$ ), 445 nm ( $\epsilon = 30410$ ), 723 nm ( $\epsilon = 380$ ).

MS ( $m/z$ ): 440 (M<sup>+</sup>; bp, <sup>80</sup>Se).

IR (KBr): 2987, 2957, 2923, 2871, 1498, 1473, 1459, 1434, 1301, 1131, 1020, 751, 682 cm<sup>-1</sup>.

<sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ : 0.74 (3H, s), 0.75 (3H, s), 0.94 (3H, s), 0.95 (3H, s), 1.26 (3H, s), 1.74 (3H, s), 1.75-1.83 (4H, m), 2.01-2.13 (4 H, m), 2.82 (1H, d,  $J = 3.9$  Hz), 3.74 (1H, d,  $J = 3.9$  Hz).

<sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$ : 12.7 (q), 14.4 (q), 18.8 (q), 19.2 (q), 19.3 (q), 19.5 (q), 24.3 (dd), 26.9 (dd), 30.6 (t), 34.0 (dd), 54.3 (s), 56.1 (s), 57.5 (d), 58.1 (d), 58.2 (s), 60.5 (s), 148.9 (s), 149.3 (s), 156.5 (s), 160.3 (s), 193.1 (s).

<sup>77</sup>Se NMR (CDCl<sub>3</sub>)  $\delta$ : 473.2, 1134.9.

Calcd for C<sub>21</sub>H<sub>28</sub>Se<sub>2</sub>: C, 57.54; H, 6.44%. Found: C, 57.36; H, 6.53%.

*X-Ray Crystallographic Data for 8.* Green platelet, orthorhombic, P2<sub>1</sub>2<sub>1</sub>2<sub>1</sub> (#19),  $a = 6.779(3)$  Å,  $b = 13.334(4)$  Å,  $c = 21.610(7)$  Å,  $V = 1953(1)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_{\text{calc}} = 1.491$  g/cm<sup>3</sup>,  $\mu(\text{MoK}\alpha) = 37.85$  cm<sup>-1</sup>,  $R = 0.061$ ,  $R_w = 0.027$ . The data were deposited in Cambridge Crystallographic Data Center (CCDC-1954441).

Selected bond lengths (Å), bond angles (deg), and torsion angles (deg) of compound **6**: Se(1)-C(1), 1.839(9); C(1)-C(2), 1.39(1); C(1)-C(5), 1.42(1); C(2)-C(3), 1.37(1); C(4)-C(5),

1.39(2); Se(2)-C(3), 1.846(9); Se(2)-C(4), 1.81(1); Se(1)-C(1)-C(2), 118.2(7); Se(1)-C(1)-C(5), 123.5(8); C(2)-C(1)-C(5), 118.3(9); C(1)-C(2)-C(3), 127.8(9); C(1)-C(2)-C(6), 128.5(9); C(3)-C(2)-C(6), 103.5(9); Se(2)-C(3)-C(2), 124.9(7); Se(2)-C(3)-C(9), 125.0(7); C(2)-C(3)-C(9), 109.8(9); Se(2)-C(4)-C(5), 127.7(8); Se(2)-C(4)-C(17), 124.1(8); C(5)-C(4)-C(17), 108.2(9); C(1)-C(5)-C(4), 123.8(9); C(1)-C(5)-C(14), 131(1); C(4)-C(5)-C(14), 103.7(9); C(3)-Se(2)-C(4), 95.2(4); Se(1)-C(1)-C(2)-C(3), 166(1); Se(1)-C(1)-C(2)-C(6), -9(2); Se(1)-C(1)-C(5)-C(4), -160.3(8); Se(1)-C(1)-C(5)-C(14), 4(2); Se(2)-C(3)-C(2)-C(1), -1(2); Se(2)-C(3)-C(2)-C(6), 175.6(8); Se(2)-C(3)-C(9)-C(8), -104(1); Se(2)-C(3)-C(9)-C(10), 151.4(8); Se(2)-C(3)-C(9)-C(13), 22(1); Se(2)-C(4)-C(5)-C(1), -11(2); Se(2)-C(4)-C(5)-C(14), -178.9(7); Se(2)-C(4)-C(17)-C(16), 106.4(9); Se(2)-C(4)-C(17)-C(18), -147.1(8); C(1)-C(2)-C(3)-C(9), -174(1); C(1)-C(2)-C(6)-C(7), 103(1); C(1)-C(2)-C(6)-C(10), -151(1); C(1)-C(5)-C(4)-C(17), 167(1); C(1)-C(5)-C(14)-C(15), -93(1); C(1)-C(5)-C(14)-C(18), 161(1); C(1)-C(5)-C(14)-C(21), 33(2); C(2)-C(1)-C(5)-C(4), 18(2); C(2)-C(1)-C(5)-C(14), -178(1); C(2)-C(3)-Se(2)-C(4), 7(1); C(2)-C(3)-C(9)-C(8), 69(1); C(2)-C(3)-C(9)-C(10), -35(1); C(2)-C(3)-C(9)-C(13), -165(1); C(2)-C(6)-C(7)-C(8), 69(1); C(2)-C(6)-C(10)-C(9), -50(1); C(2)-C(6)-C(10)-C(11), -171(1); C(2)-C(6)-C(10)-C(12), 64(1); C(3)-Se(2)-C(4)-C(5), -1(1); C(3)-Se(2)-C(4)-C(17), -178.8(8); C(3)-C(2)-C(1)-C(5), -12(2); C(3)-C(2)-C(6)-C(7), -73(1); C(3)-C(2)-C(6)-C(10), 32(1); C(3)-C(9)-C(8)-C(7), -68(1); C(3)-C(9)-C(10)-C(6), 49.5(9); C(3)-C(9)-C(10)-C(11), 168(1); C(3)-C(9)-C(10)-C(12), -66(1); C(4)-Se(2)-C(3)-C(9), 179.0(9); C(4)-C(5)-C(14)-C(15), 73(1); C(4)-C(5)-C(14)-C(18), -32(1); C(4)-C(5)-C(14)-C(21), -161(1); C(4)-C(17)-C(16)-C(15), 70(1); C(4)-C(17)-C(18)-C(14), -50.3(9); C(4)-C(17)-C(18)-C(19), -169.6(9); C(4)-C(17)-C(18)-C(20), 65(1); C(5)-C(1)-C(2)-C(6), 172(1); C(5)-C(4)-C(17)-C(16), -72(1); C(5)-C(4)-C(17)-C(18), 35(1); C(5)-C(14)-C(15)-C(16), -69(1); C(5)-C(14)-C(18)-C(17), 49.5(9).

*Procedure for mCPBA Oxidation of 1,6,6aλ<sup>4</sup>-Triselenapentalene 6.* A 30 mL CHCl<sub>3</sub> solution of 1,6,6aλ<sup>4</sup>-triselenapentalene **6** (52 mg, 0.1 mmol) was treated with *m*CPBA (70%, 74 mg, 0.30 mmol) at room temperature for 30 minutes. Then, the reaction was quenched by addition of an excess amount of saturated Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution, and saturated NaHCO<sub>3</sub> solution was added to the reaction mixture. The reaction mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub>, and the organic layer was washed with water and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> powder. After removing the solvent *in vacuo*, the crude product was purified using column chromatography on silica gel to afford 1,2-diselenole **11** (37 mg, 81% yield) as orange crystals along with 4*H*-selenopyran-4-one **10** (trace) as a pale yellow oil.

*General Procedure for Aerobic Oxidation of 4*H*-Selenopyran-4-Selones (7, 8).* A CHCl<sub>3</sub> solution of symmetrical or unsymmetrical 4*H*-selenopyran-4-selone (**7** or **8**, 1.00 mmol) was standing at room temperature for 1 week, and the reaction mixture was

filtered to remove the elemental selenium. Then, the solvent of the filtrate was removed *in vacuo*. The crude product was purified using column chromatography on silica gel to afford the corresponding 4*H*-selenopyran-4-one **9** or **10**, respectively, in quantitative yields.

### Physical and Spectral Data for 1,2-Diselenole **11**

Orange needles.

MP: 164.8°C-165.6°C

$[\alpha]_D^{20} = -17.6^\circ$  (*c* 0.1, CHCl<sub>3</sub>).

UV (CHCl<sub>3</sub>) λ<sub>max</sub>: 248 nm (ε = 18550), 438 nm (ε = 9590), 464 nm (ε = 11450).

MS (*m/z*): 456 (M<sup>+</sup>; bp, <sup>80</sup>Se), 41 (46%).

IR (KBr): 2957, 2869, 1714, 1631, 1496, 1340, 1260, 1221, 1108, 1076 cm<sup>-1</sup>.

<sup>1</sup>H NMR (CDCl<sub>3</sub>) δ: 0.73 (3H, s), 0.83 (3H, s), 0.93 (3H, s), 0.95 (3H, s), 1.15 (3H, s), 1.22 (3H, s), 1.24-1.26 (4H, m), 1.56-1.84 (2 H, m), 1.92-2.17 (2H, m), 3.03 (1H, d, *J* = 3.7 Hz), 3.05 (1H, d, *J* = 3.8 Hz).

<sup>13</sup>C NMR (CDCl<sub>3</sub>) δ: 9.1 (q), 12.9 (q), 19.0 (q), 19.6 (q), 20.1 (q), 20.3 (q), 25.4 (dd), 26.3 (dd), 30.4 (dd), 32.9 (dd), 51.1 (s), 51.3 (d), 54.3 (d), 56.7 (s), 58.6 (s), 60.5 (s), 129.5 (s), 147.3 (s), 151.8 (s), 173.2 (s), 204.5 (s).

<sup>77</sup>Se NMR (CDCl<sub>3</sub>) δ: 402.2, 889.2.

Calcd for C<sub>21</sub>H<sub>28</sub>OSe<sub>2</sub>: C, 55.51; H, 6.21%. Found: C, 55.33; H, 6.45%.

### Physical and Spectral Data for Symmetrical 4*H*-Selenopyran-4-One **9**

Pale yellow oil.

MS (*m/z*): 376 (M<sup>+</sup>; 31%, <sup>80</sup>Se), 320 (M<sup>+</sup>-CO-C<sub>2</sub>H<sub>4</sub>; 8%, <sup>80</sup>Se), 81 (bp).

IR (KBr): 2955, 2924, 2854, 1732, 1595, 1461, 1377, 1269, 1123 cm<sup>-1</sup>.

<sup>1</sup>H NMR (CDCl<sub>3</sub>) δ: 0.74 (6H, s) 0.92 (6H, s), 1.21 (6H, s), 1.76-1.81 (4H, m), 1.98-2.03 (4 H, m), 3.32 (1H, d, *J* = 3.7 Hz).

Calcd for C<sub>21</sub>H<sub>28</sub>OSe: C, 67.19; H, 7.52%. Found: C, 66.81; H, 7.34%.

### Physical and Spectral Data for Unsymmetrical 4*H*-Selenopyran-4-One **10**

Pale yellow solid.

MP: 117.9°C-118.7°C

MS (*m/z*): 376 (M<sup>+</sup>; bp, <sup>80</sup>Se), 348 (M<sup>+</sup>-CO; 68%, <sup>80</sup>Se).

IR (KBr): 2955, 2925, 2873, 1736, 1579, 1458, 1385, 1371, 1102 cm<sup>-1</sup>.

<sup>1</sup>H NMR (CDCl<sub>3</sub>) δ: 0.76 (3H, s) 0.77 (3H, s), 0.87 (3H, s), 0.91 (3H, s), 1.19 (3H, s), 1.51 (3H, s), 1.71-1.78 (4H, m), 1.97-2.03 (4 H, m), 2.76 (1H, d, *J* = 3.9 Hz), 3.24 (1H, d, *J* = 3.7 Hz).

Calcd for C<sub>21</sub>H<sub>28</sub>OSe: C, 67.19; H, 7.52%. Found: C, 66.77; H, 7.38%.

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