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Reaction of Ketone Hydrazones with Diselenium Dihalides: Simple Synthesis of Δ^3-1,3,4-Selenadiazolines and 2,5-Diarylselenophenes

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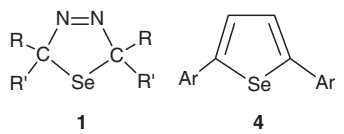
Sterically congested *cis*- and *trans*-Δ^3-1,3,4-selenadiazolines were isolated by one-pot reactions of ketone hydrazones with diselenium dibromide, which suggested the in situ formation of selone and diazoalkane intermediates. The thermolysis of these compounds gave symmetrical olefins, whereas oxidation afforded the corresponding azines. The reaction of acetophenone hydrazones with diselenium dibromide afforded 2,5-diarylselenophenes in moderate yields. The reaction proceeded through selone intermediates.

Sterically congested Δ^3-1,3,4-selenadiazolines **1** and Δ^3-1,3,4-thiadiazolines are interesting compounds for their synthetic application of sterically crowded olefins.[1] It has been reported that the reactions of sterically hindered selones **2** with sterically hindered diazoalkanes **3** afford **1**, which are decomposed to the corresponding symmetrical olefins via thermal twofold extrusion.[1,2] 2,5-Diarylselenophenes **4** are synthesized by reacting 1,3-diynes with hydrogen selenide[3] and arylacetylenes with 1,2,3-selenadiazoles,[4] by the high-temperature reaction of acetophenone anil with elemental selenium,[5] and by treating titanocycle with selenium diselenocyanate[6] (Scheme 1).

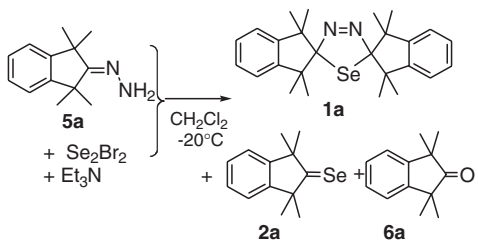


Scheme 1.

However, there has been no report on the synthesis of **4** from ketone hydrazones **5**. Recently, we reported in a communication the synthesis of Δ^3-1,3,4-selenadiazolines **1** by reacting ketone hydrazones **5** with diselenium dibromide.[7] We report herein on the full details concerning the reaction of **5** with diselenium dibromide and the synthesis of **4**.

Results and Discussion

Synthesis and Reaction of 1,3,4-Selenadiazolines. Δ^3-1,3,4-Selenadiazolines **1** have been synthesized by reacting selenoketones with diazoalkanes.[2] Selenoketones **2**, however, are generally unstable and difficult to isolate.[1] Barton and coworkers suggested the formation of **1** as an intermediate in the synthesis of sterically crowded alkenes by the reaction of benzophenone phosphoranylidene hydrazone with elemental selenium.[2] Okazaki et al. also suggested the formation of diazoalkane intermediates from the reaction of ketone hydrazones **5** with diselenium dichloride. They also reported on the one-pot synthesis of Δ^3-1,3,4-telluradiazoline by the reaction of ketone hydrazones with tellurium dichloride.[8] If the reaction of ketone hydrazones with diselenium dihalide gives not only selones **2**, but also diazoalkanes **3**, Δ^3-1,3,4-selenadiazoline **1** will be formed in a one-pot operation. To confirm this possibility, we first attempted the reaction of 1,1,3,3-tetramethylindan-2-one hydrazones (**5a**) with diselenium dibromide.



Scheme 2.

Treatment of **5a** with diselenium dibromide at −20 °C resulted in the formation of dispiro[1,1,3,3-tetramethylindane-2-2′-(Δ^3-1′,3′,4′-selenadiazoline)-5′,2″-(1″,1″,3″,3″-tetramethylindane)] (**1a**) (53%) along with 1,1,3,3-tetramethylindane-2-selone (**2a**) (10%), and 1,1,3,3-tetramethylindan-2-one (**6a**) (5%) (Scheme 2). When the reaction was carried out at rt, selone **2a** was obtained in 55% yield. Thus, temperature plays an important role in the formation of **1a** (Table 1).

The structure of **1a** was confirmed by NMR and X-ray crystallographic analyses (Fig. 1, Table 2).[9] In contrast to the structure of other five-membered heterocyclic compounds, such as 1,2,4-trithiolanes,[10] the selenadiazoline ring in **1a** is planar and approximately perpendicular to the indane rings. This structure is similar to that of 1,3,4-telluradiazoline.[11]

At −20 °C, the yield of **1a** was improved, whereas selone **2a** was obtained in moderate yield at elevated temperature. Actually, two groups have reported on the synthesis of sterically crowded selones by reacting ketone hydrazones with diselenium dihalides at elevated temperature. Guziec and Moustakis

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Table 1. Reaction of **5a** with Diselenium Dibromide

Conditions		Products (Yield/%)			
Temp/°C	Time/h	**1a**	**2a**	**6a**	Recovered **5a**
−78	5	10	8	1	75
−40	3	26	10	1	50
−30	2	34	11	2	25
−20	2	53	10	5	0
0	2	3	55	7	0
rt	1	5	55	9	0
reflux	1	0	72	5	0

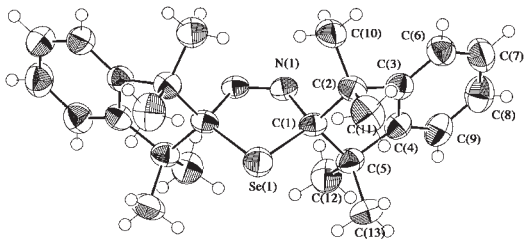


Fig. 1. X-ray crystallographic structure of **1a**.

Table 2. Selected Distances and Angles of **1a**

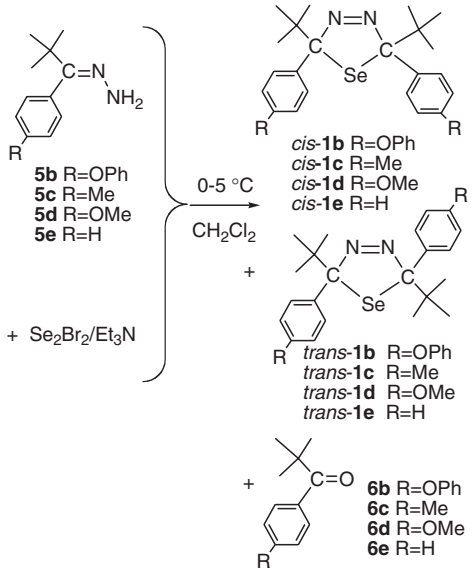
Bond length (Å)	Se–C1	1.972(3)
	N1–N1	1.234(4)
	N1–C1	1.488(3)
Bond angle (°)	C1–Se–C1	88.4(1)
	N1–N1–C1	120.6(1)
	N1–C1–Se1	105.2(2)

synthesized **2a** by reacting **5a** with diselenium dibromide in the presence of triethylamine at 50 °C.[12] Okazaki et al. reported the synthesis of **2a** by reacting diselenium dichloride with the Grignard reagent of **5a** in refluxing benzene.[13]

We next attempted the reaction of pivalophenone hydrazones with diselenium dibromide. Treatment of *p*-phenoxypivalophenone hydrazone (**5b**) with diselenium dibromide in the presence of triethylamine at 0 °C resulted in the formation of *cis*-2,5-di-*t*-butyl-2,5-di-*p*-phenoxyphenyl-Δ^3-1,3,4-selenadiazoline (*cis*-**1b**), *trans*-2,5-di-*t*-butyl-2,5-di-*p*-phenoxyphenyl-Δ^3-1,3,4-selenadiazoline (*trans*-**1b**), and *p*-phenoxypivalophenone (**6b**) (Scheme 3). The structures of *cis*-**1b** and *trans*-**1b** were confirmed from their ^{1}H NMR spectra and elemental analyses. The chemical shift of the *tert*-butyl group of *trans*-**1b** (0.89 ppm) is higher than that of *cis*-**1b** (1.19 ppm), whereas the chemical shifts of the aromatic group of *trans*-**1b** (6.91 and 7.01 ppm) are lower than those of *cis*-**1b** (6.57 and 6.80 ppm). These observations suggest that the aromatic plane of *cis*-**1b** is on the other side of the aromatic plane, whereas the *tert*-butyl group of *trans*-**1b** is on the aromatic plane. Other reactions were carried out in a similar manner (Table 3).

The reaction of 2,2,5,5-tetramethylcyclopentanone hydrazone (**5f**) with diselenium dibromide in the presence of triethylamine also afforded dispiro[2,2,5,5-tetramethylcyclopentane-1,2′-(Δ^3-1′,3′,4′-selenadiazoline)-5″,1″-(2″,2″,5″,5″-tetramethylcyclopentane)] (**1f**) in 43% yield (Scheme 4).

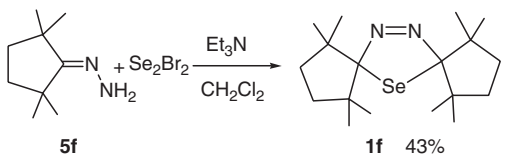
The postulated mechanism for this reaction is depicted in



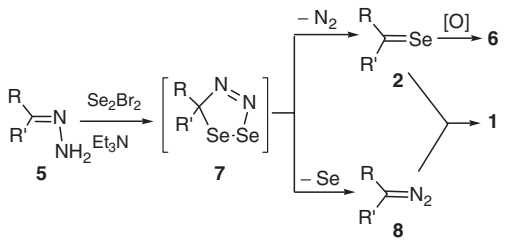
Scheme 3.

Table 3. Reaction of Pivalophenone Hydrazones **5b**–**5e** with Diselenium Dibromide

Hydrazone **5**	Temp/°C	Products (Yield/%)				
		cis-**1**	*trans*-**1**		**6**	
5b	0	**1b**	7	77	**6b**	5
5b	rt	**1b**	trace	52	**6b**	15
5c	0	**1c**	5	58	**6c**	15
5d	0	**1d**	2	60	**6d**	10
5e	0	**1e**	trace	56	**6e**	18

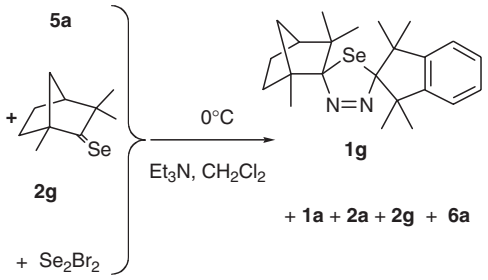


Scheme 4.

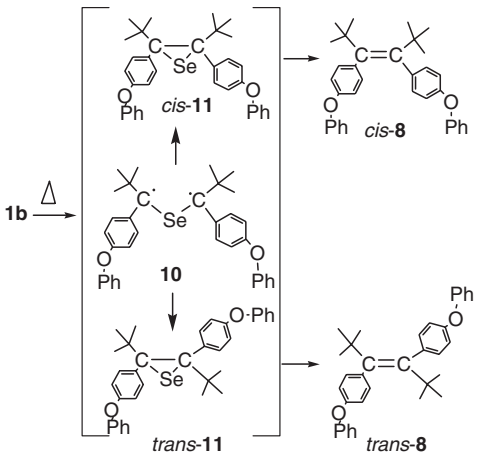


Scheme 5.

Scheme 5. The anion of **5** reacts with diselenium dibromide to afford 1,2,3,4-diselenadiazoline **7**. The extrusion of selenium from **7** affords diazoalkane **3** (minor route), whereas N_2 is extruded to afford the selone **2** (major route). Selenadiazoline **1** is formed by the 1,3-dipolar cycloaddition reaction of **2** with **3**, both generated in situ, as shown in Scheme 5. The proposed mechanism is similar to that of 1,2,4-telluradiazoline suggested by Okazaki and co-workers.[11]



Scheme 6.



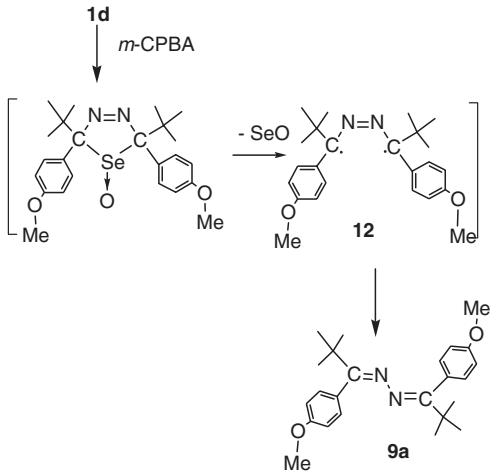
Scheme 7.

Actually, when the reaction of **5a** with diselenium dibromide was carried out in the presence of 1,3,3-trimethylnorbornane-2-selone (**2g**), unsymmetrical 1,3,4-selenadiazoline **1g** was obtained in 7% yield along with symmetrical selenadiazoline **1a** (25%) and indane-2-selone **2a** (15%), suggesting that the intermediates of this reaction are diazoalkane **3** and selone **2** (Scheme 6).

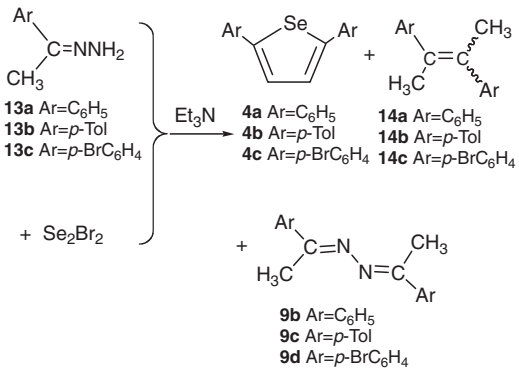
Since *cis*- and *trans*-1,3,4-selenadiazolines **1b**–**1e** were isolated, we attempted the thermolysis of **1b** to confirm the reaction mechanism of the twofold extrusion. Heating *trans*-**1b** up to 170 °C resulted in the formation of *cis*-olefin (*cis*-**8**, 7%) and *trans*-olefin (*trans*-**8**, 70%), whereas the thermolysis of *cis*-**1b** gave *cis*-**8** (33%) and *trans*-**8** (66%). These results suggested that the reaction might proceed through biradical intermediates. Heating of **1b** resulted in the extrusion of nitrogen to afford biradical **10**, which recombined to give episelenide **11**. Episelenide **11** is too unstable to isolate, affording *cis*-**8** and *trans*-**8**. The biradical intermediate **10** equilibrates to a more stable conformer, resulting in the formation of both isomers (Scheme 7).

An alternative route that includes the initial extrusion of selenium is excluded by the following result. The oxidation of *trans*-**1d** with *m*-CPBA at room temperature resulted in the formation of *p*-methoxypivalophenone azine **9a** (50%) and *p*-methoxypivalophenone hydrazone **5d** (30%), suggesting that the initial fission of the carbon–selenium bond of selenoxide affords biradical **12**, which easily isomerizes to azine **9a** (Scheme 8).

Synthesis of 2,5-Diarylselenophenes. Because eneselenol is more stable than the corresponding selone,[14] the reaction of



Scheme 8.



Scheme 9.

enolizable ketone hydrazones with diselenium dibromide is the next topic of interest. Treatment of acetophenone hydrazone (**13a**) with diselenium dibromide in refluxing benzene resulted in the formation of 2,5-diphenylselenophene (**4a**) in 58% yield along with 2,3-diphenyl-2-butene (*E*- and *Z*-**14a**) (Scheme 9).

When the reaction was carried out at 20 °C, acetophenone azine (**9b**) was isolated in 13% yield along with **4a** and **13a**. The other reactions are shown in Table 4.

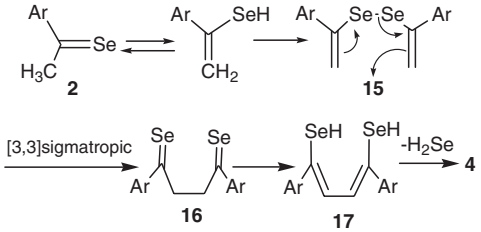
The formation of alkene **14a** can be explained by the thermal twofold extrusion of unstable 1,3,4-selenadiazoline.[2] Then, how can we account for the formation of selenophene **4**? The initially formed 1-phenylethaneselone (**2**) partially isomerizes to eneselenol, which is easily oxidized to the corresponding diselenide **15**. A 3,3-sigmatropic rearrangement resulted in the formation of diselone **16**, which again isomerized to another type of eneselenol **17**. Hydrogen selenide abstraction of **17** finally gave selenophene **4** (Scheme 10).

To confirm the formation of **15**, we then performed the reaction of 2-methyl-1-phenylpropan-1-one (isobutyrophenone) hydrazone (**13d**) with diselenium dibromide. When the reaction was carried out in refluxing benzene, the corresponding alkenyl diselenide **15** was obtained in 42% yield along with a mixture of *E*- and *Z*-2,5-dimethyl-3,4-diphenyl-3-hexene (**14d**) (Scheme 11).

Although the detailed reaction mechanism remains to be clarified, this is the first example of the formation of 2,5-di-

Table 4. Reaction of Acetophenone Hydrazones **13** with Diselenium Dibromide

Hydrazone		Solvent	Temp/°C	Products (Yields/%)					
13	Ar			**4**		**14**		**9**	
13a	C_6H_5	Dichloromethane	−20	**4a**	25	**14a**	33	**9b**	20
13a	C_6H_5	Benzene	20	**4a**	34	**14a**	33	**9b**	20
13a	C_6H_5	Benzene	60	**4a**	45	**14a**	33	**9b**	20
13a	C_6H_5	Benzene	reflux	**4a**	58	**14a**	33	**9b**	20
13a	C_6H_5	THF	reflux	**4a**	51	**14a**	30	**9b**	15
13b	*p*-Tol	Benzene	reflux	**4b**	48	**14b**	20	**9c**	15
13c	*p*-BrC_6H_4	Benzene	reflux	**4c**	39	**14c**	25	**9d**	20



Scheme 10.

arylselenophene **4** from acetophenone hydrazone **13**.

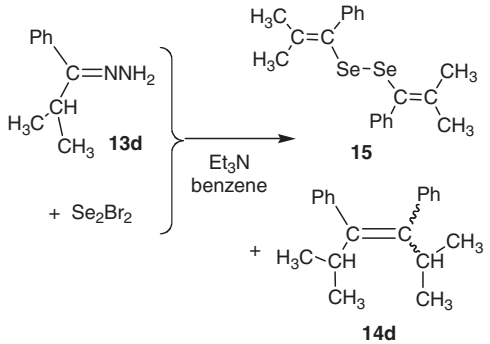
In summary, we synthesized 1,3,4-selenadiazoline **1** by reacting ketone hydrazone **5** with diselenium dibromide. When acetophenone hydrazones were used as substrates, 2,5-diarylselenophenes were obtained in moderate yields.

Experimental

General. All chemicals were obtained from commercial suppliers and were used without further purification. Analytical TLC was carried out on precoated plates (Merck silica gel 60, F254) and flash column chromatography was performed with silica (Merck, 70–230 mesh). NMR spectra (^{1}H at 400 MHz; ^{13}C at 100 MHz) were recorded in $CDCl_3$ solvent, and the chemical shifts were expressed in ppm relative to internal TMS. The melting points were uncorrected.

Material. Ketone hydrazones **5a–f** were prepared by the reaction of ketones with hydrazine monohydrate.[2a,b,12] Acetophenone hydrazones **13a–d** were synthesized by a method from the literature.[15] Selone **2g** was synthesized by a method from the literature.[2b]

Reaction of 1,1,3,3-Tetramethylindan-2-one Hydrazone 5a with Diselenium Dibromide. To a solution of indan-2-one hydrazone **5a** (0.40 g, 2.0 mmol) and triethylamine (0.61 g, 6.0 mmol) in dichloromethane (15 mL) was added dropwise a solution of diselenium dibromide (0.80 g, 2.2 mmol) in dichloromethane (10 mL) at −20 °C. After stirring for 3 h, the reaction mixture was poured into water, separated, and extracted from dichloromethane (10 mL × 2). The combined extract was dried over magnesium sulfate, filtered, and evaporated to give a brown solid, which was chromatographed over silica gel by elution with hexane–dichloromethane (1:1). Dispiro[1,1,3,3-tetramethylindane-2-2′-(Δ^3-1′,3′,4′-selenadiazoline)-5′,2″-(1″,1″,3″,3″-tetramethylindane)] (**1a**) was eluted first (0.24 g, 0.53 mmol). **1a**: mp 170–171 °C (lit.[16] mp 170 °C). 1,1,3,3-Tetramethylindane-2-selone (**2a**) (0.050 g, 0.20 mmol): mp 39–42 °C (lit.[17] mp 40–43 °C), and 1,1,3,3-tetramethylindan-2-one (**6a**) (0.019 g, 0.10 mmol) were obtained.



Scheme 11.

Reaction of *p*-Phenoxypivalophenone Hydrazone 5b with Diselenium Dibromide. To a solution of *p*-phenoxypivalophenone hydrazone **5b** (0.536 g, 2.0 mmol) and triethylamine (0.88 g, 8.0 mmol) in dichloromethane (20 mL) was added a solution of diselenium dibromide (0.80 g, 2.2 mmol) in dichloromethane (10 mL) at 0 °C. After stirring for 3 h, the reaction mixture was poured into water, separated, and extracted from dichloromethane. The combined extract was dried over magnesium sulfate, filtered, and evaporated to give a brown solid, which was chromatographed over silica gel by elution with hexane–dichloromethane (1:1). A mixture of *cis*- and *trans*-2,5-di-*t*-butyl-2,5-bis(*p*-phenoxyphenyl)-Δ^3-1,3,4-selenadiazoline (**1b**) was obtained first. Pivalophenone **6b** was obtained second (0.025 g, 0.02 mmol). The mixture was subjected to gel HPLC to give pure *trans*-**1b** (0.45 g, 0.77 mmol) and *cis*-**1b** (0.041 g, 0.070 mmol). *cis*-**1b**: mp 118–119 °C. ^{1}H NMR ($CDCl_3$) δ 1.19 (s, 18H, *tert*-Bu), 6.57 (d, 4H, J = 9 Hz, Ar), 6.80 (d, 4H, J = 9 Hz, Ar), 7.05 (m, 2H, Ph), 7.13 (m, 4H, Ph), 7.32 (m, 4H, Ph). ^{13}C NMR ($CDCl_3$) δ 28.31 (*t*-Bu), 40.38 (q-C), 116.63, 118.40, 121.31 (spiro-C), 122.89, 129.45, 129.57, 135.67, 155.35, 157.01 (Ar). Found: C, 70.36; H, 6.21; N, 5.11%. Calcd for $C_{34}H_{36}N_2O_2Se$: C, 69.97; H, 6.22; N, 4.80%. *trans*-**1b**: mp 162–163 °C. ^{1}H NMR ($CDCl_3$) δ 0.89 (s, 18H, *tert*-Bu), 6.91 (d, 4H, J = 8.0 Hz, Ar), 7.01 (d, 4H, J = 8.0 Hz, Ar), 7.11 (m, 2H, Ph), 7.34 (m, 4H, Ph), 7.52 (m, 4H, Ph). ^{13}C NMR ($CDCl_3$) δ 27.64 (*t*-Bu), 41.62 (q-C), 116.94, 118.91, 123.26, 126.52 (spiro-C), 129.52, 129.56, 137.52, 156.05, 156.68 (Ar). Found: C, 69.93; H, 6.03; N, 4.44%. Calcd for $C_{34}H_{36}N_2O_2Se$: C, 69.97; H, 6.22; N, 4.80%.

Other reactions were carried out in a similar manner. *cis*-**1c**: mp 104–105 °C. ^{1}H NMR ($CDCl_3$) δ 1.16 (s, 18H, *tert*-Bu), 2.09 (s, 6H, Me), 6.66 (d, 4H, J = 8.4 Hz, Ar), 7.00 (d, 4H, J = 8.4 Hz, Ar). ^{13}C NMR ($CDCl_3$); δ 20.64 (Me), 28.26 (*t*-Bu), 40.37 (q-C), 121.86, 126.77 (spiro-C), 127.95, 135.89, 137.84 (Ar). Found: C, 67.09; H, 7.93; N, 6.61%. Calcd for $C_{24}H_{32}N_2Se$: C, 67.43; H,

7.55; N, 6.55%. *trans*-**1c**: mp 181–182 °C. ^{1}H NMR ($CDCl_3$) δ 0.86 (s, 18H, *tert*-Bu), 2.33 (s, 6H, Me), 7.06 (d, 4H, $J = 8.0$ Hz, Ar), 7.43 (d, 4H, $J = 8.0$ Hz, Ar). ^{13}C NMR ($CDCl_3$) δ 21.13 (Me), 27.34 (*tert*-Bu), 41.45 (q-C), 126.53 (spiro-C), 127.51, 128.15, 136.51, 139.81 (Ar). Found: C, 67.38; H, 7.55; N, 6.81%. Calcd for $C_{24}H_{32}N_2Se$: C, 67.43; H, 7.55; N, 6.55%. *cis*-**1d**: mp 102–104 °C. ^{1}H NMR ($CDCl_3$) δ 1.15 (s, 18H, *t*-Bu), 3.81 (s, 6H, OMe), 6.41 (d, 4H, $J = 8.0$ Hz, Ar), 7.06 (d, 4H, $J = 8.0$ Hz, Ar). Found: C, 62.45; H, 7.03; N, 6.19%. Calcd for $C_{24}H_{32}N_2O_2Se$: C, 62.74; H, 7.02; N, 6.10%. *trans*-**1d**: mp 124–125 °C. ^{1}H NMR ($CDCl_3$) δ 0.86 (s, 18H, *t*-Bu), 3.81 (s, 6H, OMe), 6.80 (d, 4H, $J = 8.8$ Hz, Ar), 7.48 (d, 4H, $J = 8.8$ Hz, Ar). ^{13}C NMR ($CDCl_3$) δ 27.49 (*t*-Bu), 41.49 (q-C), 55.10 (OMe), 112.24, 126.58 (spiro-C), 129.44, 135.17, 158.45 (Ar). Found: C, 62.95; H, 6.86; N, 6.21%. Calcd for $C_{24}H_{32}N_2O_2Se$: C, 62.74; H, 7.02; N, 6.10%. *trans*-**1e**: mp 163–164 °C. ^{1}H NMR ($CDCl_3$) δ 0.87 (s, 18H, *t*-Bu), 7.25 (m, 6H, Ar), 7.56 (br d, 4H, $J = 7.2$ Hz, Ar). ^{13}C NMR ($CDCl_3$) δ 27.50 (*t*-Bu), 41.39 (q-C), 126.84, 126.99 (spiro-C), 127.18, 128.50, 142.93 (Ph). Found: C, 66.32; H, 6.99; N, 6.27%. Calcd for $C_{22}H_{28}N_2Se$: C, 66.15; H, 7.07; N, 7.01%. *cis*-**1e** could not be isolated.

Reaction of 2,2,5,5-tetramethylcyclopentanone hydrazone (**5f**) with diselenium dibromide was carried out in a similar manner. Dispiro[2,2,5,5-tetramethylcyclopentane-1,2′-(Δ^3-1′,3′,4′-selenadiazoline)-5″,1″-(2″,2″,5″,5″-tetramethylcyclopentane)] (**1f**): mp 125–126 °C (lit.[16] mp 126–127 °C).

Reaction of 5a with Diselenium Dibromide in the Presence of Selenofenchone (2g). To a solution of **5a** (0.40 g, 2.0 mmol), (1*S*)-1,3,3-trimethylbicyclo[2.2.1]heptane-2-selone (**2g**) (0.43 g, 2.0 mmol), and triethylamine (0.88 g, 8.0 mmol) in dichloromethane (20 mL) was added a solution of diselenium dibromide (0.80 g, 2.2 mmol) in dichloromethane (10 mL) at −20 °C. After stirring for 2 h, the reaction mixture was poured into water, separated, and extracted from dichloromethane. The combined extract was dried over magnesium sulfate, filtered, and evaporated to give brown solid, which was chromatographed over silica gel by elution from hexane–dichloromethane (1:1). 1,1,3,3-Tetramethylindane-2-selone (**2a**) (0.075 g, 0.30 mmol) was obtained first. Selenadiazolines **1a** (0.085 g, 0.25 mmol) and **1g** (0.029 g, 0.07 mmol) were eluted second. Compound **1g**: yellow crystals, mp 172–174 °C. (lit.[17] mp 125–128 °C). ^{1}H NMR ($CDCl_3$) δ 0.93 (s, 3H, Me), 0.97 (s, 3H, Me), 1.03 (s, 3H, Me), 1.10 (s, 3H, Me), 1.16 (s, 3H, Me), 1.40 (s, 3H, Me), 1.42 (s, 3H, Me), 1.45–1.52 (m, 4H, CH_2), 1.80 (br, 1H, CH), 1.99 (br s, 1H, CH), 2.77 (br d, 1H, $J = 10.0$ Hz, CHH), 7.19–7.25 (m, 4H, Ar). ^{13}C NMR ($CDCl_3$) δ 18.98 (Me), 23.14 (Me), 25.24 (Me), 26.04 (Me), 29.88 (Me), 33.29 (Me), 33.74 (Me), 36.72, 42.41, 48.05, 49.51, 51.76, 57.14, 122.47, 122.85 (spiro-C), 127.21, 127.26, 128.34, 148.41, 148.78. 1,1,3,3,-Tetramethylindan-2-one (**6a**) was finally obtained (0.038 g, 0.20 mmol).

Thermolysis of Δ^3-1,3,4-Selenadiazoline 1b. *trans*-Selenadiazoline **1b** (59 mg, 0.10 mmol) was heated at 180 °C for 10 min. The reaction mixture was dissolved into dichloromethane and filtered. The solution was evaporated to give *cis*- and *trans*-2,2,5,5-tetramethyl-3,4-bis(*p*-phenoxyphenyl)-3-hexene (**8**) (1:3) in 85% yield. The mixture was subjected to gel-HPLC to afford *cis*-**8** (3.0 mg, 0.007 mmol). mp 108–110 °C. ^{1}H NMR ($CDCl_3$) δ 1.27 (s, 18H, *t*-Bu), 6.27 (s, 8H, Ar), 6.76 (d, 4H, $J = 7.6$ Hz, OPh), 7.00 (t, 2H, $J = 7.6$ Hz, OPh), 7.26 (t, 4H, $J = 7.6$ Hz, OPh). Found: C, 85.44; H, 7.30%. Calcd for $C_{34}H_{36}O_2$: C, 85.67; H, 7.61%. *trans*-**8** (33 mg, 0.070 mmol): mp 159.5–160.5 °C. ^{1}H NMR ($CDCl_3$) δ 0.75 (s, 18H, *t*-Bu), 6.95 (d, 4H, $J = 8.0$ Hz, Ar), 7.04 (d, 4H, $J = 8.0$ Hz, OPh), 7.09 (t, 2H, $J = 7.6$ Hz, OPh), 7.12 (d, 4H, $J = 8.0$ Hz, Ar), 7.34 (t, 4H, $J = 7.6$ Hz, OPh). Found: C, 85.48; H, 7.64%. Calcd for $C_{34}H_{36}O_2$: C, 85.67; H, 7.61%.

Oxidation of Δ^3-1,3,4-Selenadiazoline 1d. To a solution of *trans*-1,3,4-Δ^3-selenadiazoline **1d** (59 mg, 0.1 mmol) in chloroform (5 mL) was added a solution of *m*-chloroperbenzoic acid (85%, 61 mg, 0.3 mmol) in chloroform (5 mL) at rt. After being stirred for 2 h, the reaction mixture was filtered and evaporated to give dark yellow solid, which was chromatographed over silica gel by elution with hexane–dichloromethane to afford yellow crystals of azine **9a** (20 mg, 0.05 mmol) and *p*-methoxypivalophenone (11 mg, 0.056 mmol). **9a**: mp 124–125 °C. ^{1}H NMR ($CDCl_3$) δ 0.92 (s, 18H, *t*-Bu), 3.82 (s, 6H, OMe), 6.87 (d, 4H, $J = 8.8$ Hz, Ar), 6.92 (d, 4H, $J = 8.8$ Hz, Ar). ^{13}C NMR ($CDCl_3$) δ 28.18 (*t*-Bu), 37.93 (q-C), 54.86 (OMe), 112.66, 128.52, 129.04, 158.41 (Ar), 164.74 (C=N). Found: C, 75.77; H, 8.76; N, 7.24%. Calcd for $C_{22}H_{28}N_2Se$: C, 75.35; H, 8.96; N, 7.32%.

Reaction of Acetophenone Hydrazone (13a) with Diselenium Dibromide. To a refluxing solution of acetophenone hydrazone **13a** (0.27 g, 2.0 mmol) and triethylamine (0.61 g, 6.0 mmol) in benzene (20 mL) was added dropwise a solution of diselenium dibromide (0.80 g, 2.2 mmol) in benzene (10 mL) at 0 °C. After refluxing for 2 h, the reaction mixture was poured into water, separated, and extracted from benzene (10 mL × 2). The combined extract was dried over magnesium sulfate, filtered, and evaporated to give a brown solid, which was chromatographed over silica gel by elution with hexane–dichloromethane (1:1). A mixture of (*E*)- and (*Z*)-2,3-diphenyl-2-butene (**14a**) (0.11 g, 0.56 mmol) was eluted first (E:Z–1:5). The spectral data (^{1}H NMR) of the mixture of **14a** were identical with the reported data.[18] 2,5-Diphenylselenophene (**4a**) was eluted next (0.33 g, 1.16 mmol). **4a**: mp 171–173 °C (lit.[19] 170–172 °C). Acetophenone azine (**9b**) was finally eluted. mp 122–123 °C. (lit.[20] 123 °C)

Another reaction was carried out in a similar manner. 2,5-di-*p*-tolylselenophene (**4b**). mp 192–194 °C (lit.[19] mp 192–194 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.35 (s, 6H), 7.15 (d, 4H, $J = 7.6$ Hz, Tol), 7.37 (s, 2H), 7.44 (d, 4H, $J = 7.6$ Hz, Tol). ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.7 (Me), 125.91, 126.20, 129.86, 133.91, 137.72, 149.65. 2,5-bis(*p*-bromophenyl)selenophene (**4c**): mp 214–216 °C (lit.[19] mp 214–216 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39–7.41 (m, 6H), 7.47–7.49 (d, 4H, Ar).

Reaction of 2-Methyl-1-phenylpropan-1-one Hydrazone (13d) with Diselenium Dibromide. To a refluxing solution of **13d** (0.16 g, 1.0 mmol) and triethylamine (0.30 g, 3.0 mmol) in benzene (15 mL) was added a solution of diselenium dibromide (0.40 g, 1.1 mmol) in benzene (8 mL). After refluxing for 2 h, the reaction mixture was poured into water, separated, and extracted from benzene (5 mL × 2). The combined extract was dried over magnesium sulfate, filtered, and evaporated to give a brown solid, which was chromatographed over silica gel by elution from hexane–dichloromethane (1:1). A mixture of (*E*)- and (*Z*)-2,5-dimethyl-3,4-diphenyl-3-hexene (**14d**) (0.055 g, 0.21 mmol) was eluted first (E:Z–3:2). The spectral data (^{1}H NMR) of the mixture of **14d** were identical with the reported data.[18] 1,2-Bis(2-methyl-1-phenyl-1-propenyl) diselenide (**15**) was obtained second. **15**: Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.56 (s, 6H, Me), 2.00 (s, 6H, Me), 6.79 (d, 4H, $J = 7.2$ Hz, Ph), 7.09–7.12 (m, 6H, Ph). ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.36 (Me), 25.50 (Me), 126.61, 126.84, 127.67, 130.14, 138.24, 142.37. MS: Found: 422.0. Calcd for $C_{20}H_{22}Se_2$: 422.0 (M^+). Elemental analysis was failed due to the small impurity of unseparable **14d**.

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