Selenobenzophenones and Diazoalkanes: Isolation of Tetraarylethylenes by the Reaction of Benzophenone Hydrazones with Diselenium Dibromide

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The reaction of selenobenzophenones with diazomethane afforded the corresponding diarylethylenes and symmetrical olefins. The reaction with diaryldiazomethanes gave three different types of tetraarylethylenes. This reaction proceeded through 1,3,4-selenadiazoline intermediates, and retrocyclization was observed. The formation of 1,3,4-selendiazolines was independently confirmed by the reaction of benzophenone hydrazones with diselenium dibromide, which afforded tetraarylethylenes in good yields. This method is applicable to the two-step synthesis of tetraarylethylenes from benzophenones.

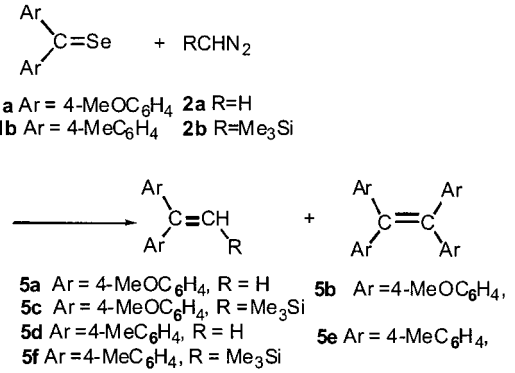
Introduction

Recently, much attention has been paid to the chemistry of carbon−selenium double bonds because of their unique and interesting reactivity.[1,2] The reaction of selenoketones **1** with diazoalkanes **2** was extensively studied by Barton and Guziec et al.[3] They isolated sterically congested **1** and reacted it with **2** to afford 1,3,4-selenadiazolines **3** in good yields. Berg et al. reported the synthesis of **3** by the reaction of carbon diselenide and di-*tert*-butyldiazomethane.[4] Recently, we have isolated *cis*- and *trans*-**3** by the reaction of sterically congested ketone hydrazones **4** with diselenium dibromide via **1** and **2** as intermediates.[5] Resonance-stabilized selenoketones, selenobenzophenones **1**, are already known to react with **2**, which finally afforded tetraarylethylenes **5** in good yields.[6] These results suggest the possibility of direct synthesis of **5** from benzophenone hydrazones. In this paper, we would like to report the synthesis of symmetrical **5** from selenobenzophenones **1**, or benzophenone hydrazones **4**.

Results and Discussion

Reaction of Isolated Selenobenzophenones with Diazoalkanes

Treatment of 4,4′-dimethoxyselenobenzophenone (**1a**) with diazomethane (**2a**) at room temperature resulted in the formation of 1,1-bis(4-methoxyphenyl)ethylene (**5a**) and tetrakis(4-methoxyphenyl)ethylene (**5b**) in 50 and 5% yields, respectively (Scheme 1). The result of this reaction is shown in Table 1.



Scheme 1

Table 1. Reaction of **1** with diazomethane **2**

1	2	Equiv.	Products (yields, %) Unsymmetrical **5**	Symmetrical **5**		
1a	**2a**	5	**5a**	50	**5b**	5
1a	**2b**	3	**5c**	62	**5b**	26
1b	**2a**	5	**5d**	48	**5e**	11
1b	**2b**	3	**5f**	9	**5e**	31

As to the formation of unsymmetrical **5**, the reaction might proceed through 1,3,4-selenadiazoline intermediates.[3] First, the reaction of selone **1a** with **2a** afforded the corresponding 1,3,4-selenadiazoline (**3a**), which converted

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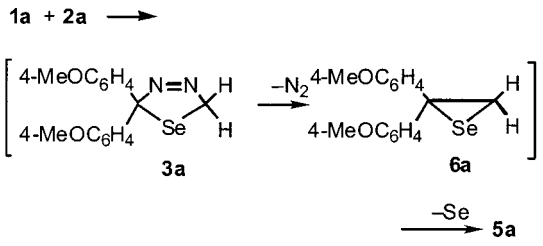
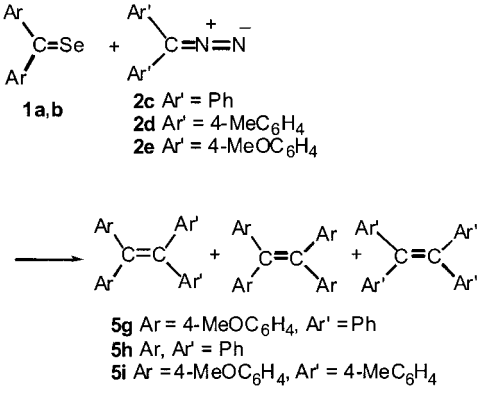
into the episelenide **6a**. Since **6a** is unstable, it decomposed to selenium and olefin **5a** (Scheme 2).



Scheme 2

However, this mechanism cannot explain the formation of symmetrical olefins **5b** and **5e**. Thus, another mechanism must have been operative. In view of the formation of the readily isolable tetraarylethylene **5** and mechanistic investigation of the above reaction, the reaction of **1a** with diphenyldiazomethane (**2c**) was carried out. Treatment of **1a** with **2c** resulted in the formation of 1,1-bis(4-methoxyphenyl)-2,2-diphenylethylene (**5g**), tetraphenylethylene (**5h**), and **5b** in 34, 10 and 33% yields, respectively. At −40 °C, nitrogen evolution was observed in this reaction, while red selenium was precipitated when the temperature rose to −20 °C (Scheme 3). The investigated reactions are summarized in Table 2.



Scheme 3

Table 2. Reaction of **1** with diaryldiazomethanes **2c**–**e**

1	2	Conditions eq.	Temp./°C	Products (yields/%) Symmetrical **5**		Unsymmetrical **5**	
1a	**2c**	1	-78-r.t.	**5b** 10	**5h** 33	**5g** 34	
1a	**2d**	1	-78-r.t.	**5b** 5	**5e** 20	**5i** 72	
1a	**2d**	1	r.t.	**5b** 10	**5e** 20	**5i** 54	
1a	**2e**	1	-45-r.t.	**5b** 84			
1b	**2e**	1.5	r.t.	**5b** 29	**5e** 31	**5i** 26	
1b	**2d**	1	r.t.		**5e** 75		

Besides the expected olefins **5g** and **5i**, symmetrical olefins **5b, 5e** and **5h** were also obtained. Thus, the reaction might proceed as follows. The reaction of 4,4′-dimethoxyselenobenzophenone (**1a**) with diphenyldiazomethane (**2c**) gave 2,2-bis(4-methoxyphenyl)-5,5-diphenyl-1,3,4-selenadiazoline (**3b**), which dissociated by a retro-1,3-dipolar reaction to selenobenzophenone (**1c**) and 4,4′-dimethoxydiphenyldiazomethane (**2e**). The obtained selenobenzophenone **1c** reacted with **2c** to afford 2,2,5,5-tetraphenyl-1,3,4-selenadiazoline (**3c**), whereas diazomethane **2e** reacted with **1a** to give another symmetrical 1,3,4-selenadiazoline **3d**. The resulting three 1,3,4-selenadiazolines **3b**, **3c** and **3d** decomposed by elimination of nitrogen to form episelenide **6**, and finally elemental selenium was precipitated to give olefins **5b**, **5g** and **5h** (Scheme 4).

The present reaction involving **1** is quite different from the reaction of thiobenzophenone with diazomethane. Thiobenzophenone was found to react with diazomethane (**2a**) to give the corresponding thiirane and 1,3-dithiolane.[7–10] The retrocyclization of 1,3,4-thiadiazoline was not observed, because thiocarbonyl ylide was a plausible intermediate in this reaction. To check the formation of selenocarbonyl ylide, the reaction of **1a** with **2a** and dimethyl acetylenedicarboxylate was carried out. If selenocarbonyl ylide was formed as an intermediate, the corresponding cycloadduct would result. The obtained products were only the corresponding olefins **5a** and **5b**, suggesting that an equilibrium between episelenide and selenocarbonyl ylide is not involved (Scheme 5).

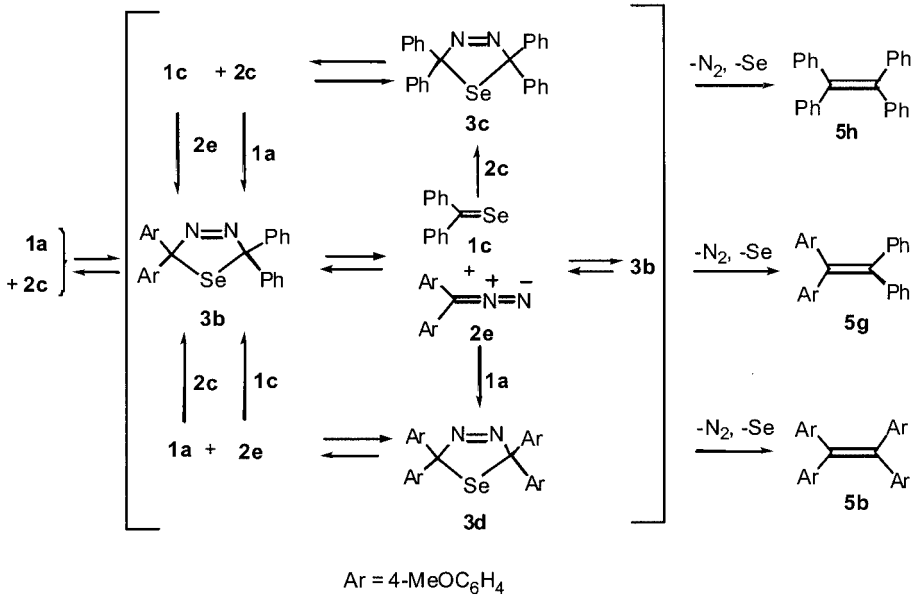
The existence of retrocyclization was supported by the following results. Back et al. found that the reaction of di-*tert*-butylselenoketone (**1d**) with **2c** afforded 5,5-diphenyl-2,2-di-*tert*-butyl-1,3,4-selenadiazoline (**3e**) in 73% yield.[3b] The partial stability of **3e** might be attributed to steric hindrance. Thermolysis of **3e** afforded only the normal decomposition product, 1,1-di-*tert*-butyl-2,2-diphenylethylene (**5j**) along with di-*tert*-butylselenoketone (**1c**) (Scheme 6).[3b] We have carefully reinvestigated this reaction to discover whether disproportionation products were formed.

When the reaction was carried out in refluxing benzene for 13 h, the obtained products were **5h**, (12%) and benzophenone (**7a**) (55%) along with the expected decomposition products **5j**, (16%) and **1d** (4%). To confirm the formation of a selenobenzophenone intermediate, the reaction of **3e** with 2,3-dimethyl-1,3-butadiene was carried out. Treatment of **3e** with 2,3-dimethylbutadiene (five equivalents) in refluxing benzene afforded the corresponding Diels–Alder adduct **8** in 62% yield (Scheme 6).

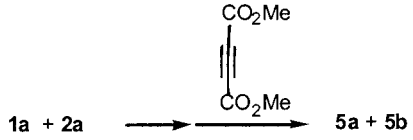
Since Guziec et al. observed retrocyclization of extremely sterically hindered **1**,[3d] the retrocyclization of 1,3,4-selenadiazolines with four aromatic groups might be a reasonable step in this reaction.

Synthesis of Tetraarylethylenes by the Reaction of Benzophenone Hydrazones with Diselenium Dibromide

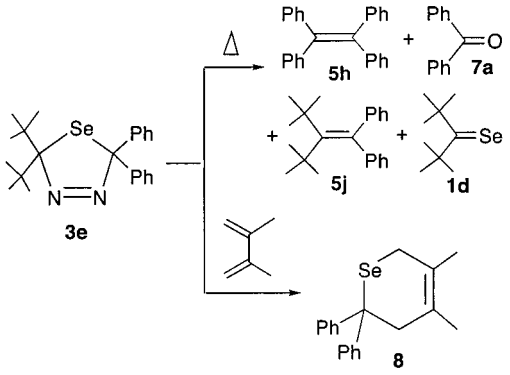
Diselenium dihalides are useful reagents for the synthesis of sterically congested selenoketones from ketone hydrazones.[11] Recently, we have found that the reaction of steri-



Scheme 4



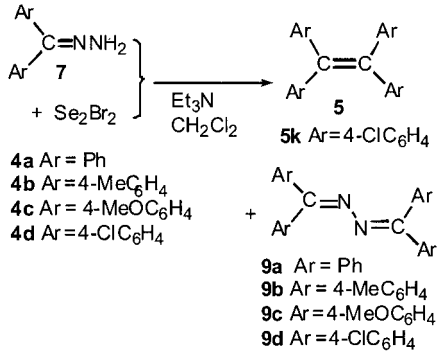
Scheme 5



Scheme 6

cally congested ketone hydrazones **4** with diselenium dibromide gave *cis*- and *trans*-1,3,4-selenadiazolines **3** in moderate yields.[5] Ishii et al. have reported that the intramolecular reaction of diketone dihydrazone with diselenium dichloride gave 1,3,4-selenadiazoline **3** as a side product.[12] These results suggested that the reaction involving ketone hydrazones **4** and diselenium dihalides gave not only selenoketones but also diazoalkanes. As previously stated, we have shown that the reaction of the selenobenzophenones **1** with diaryldiazomethanes **2** gave tetraarylethylenes **5** in good yields. The reported methods for the formation of tetraarylethylenes **5** include thermolysis of diaryl thioketones,[13] decomposition of diaryldiazomethanes by $HClO_4$,[14] reduction of tetraarylethylene sulfides,[15] reaction of diaryldiazomethanes with *o*-sulfobenzoic anhydride,[16] reaction of diaryl thioketones with Cu,[17] and ytterbium metal-mediated desulfurization and coupling reaction of diaryl thioketones.[18] However, these methods require isolation of diaryl thioketones or diaryldiazomethanes. Our desire to extend the scope of the method prompted us to examine the possibility of the formation of **5** via intermediates **3**.

Treatment of benzophenone hydrazone (**4a**) with diselenium dibromide in the presence of triethylamine at room temperature resulted in the formation of tetraphenylethylene (**5g**) in 76% yields. However, the reaction of 4,4′-dimethylbenzophenone hydrazone (**4b**) with diselenium dibromide gave tetraarylethylenes (**5e**) and 4,4′-dimethylbenzophenone azines (**9b**) in 44 and 34% yields, respectively (Scheme 7). When the present reaction was carried out in refluxing benzene, the yields of **5** were up to 82%. By using a catalytic amount of diselenium dibromide, small amount of alkenes **5** were obtained. The results are shown in Table 3.

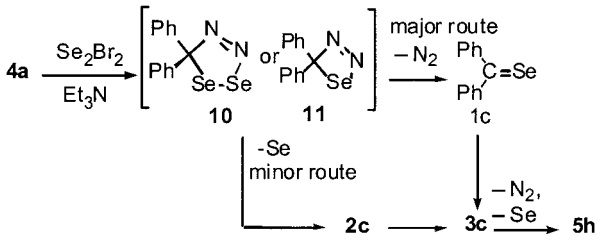


Scheme 7

Table 3. Reaction of benzophenone hydrazones **4** with diselenium dibromide

4	Ar	Conditions Solvent	Temp./°C	Time/h	Products (Yields/%) 5		9	
4a	Ph	CH_2Cl_2	r.t.	3	**5h**	72	**9a**	2
4a		benzene	reflux	2	**5h**	85	**9a**	0
4b	4-MeC_6H_4	CH_2Cl_2	r.t.	3	**5e**	44	**9b**	34
4b		benzene	reflux	2	**5e**	82	**9b**	0
4c	4-$MeOC_6H_4$	benzene	reflux	3	**5b**	66	**9c**	0
4d	4-ClC_6H_4	benzene	reflux	2	**5k**	83	**9d**	0

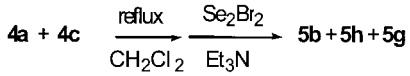
The reaction most likely proceeds as follows. The anion of benzophenone hydrazone (**4a**) reacts with diselenium dibromide to afford the 1,2,3,4-diselenadiazoline **10** or the 1,2,3-selenadiazete **11**. Loss of selenium from **10** or **11** affords diphenyldiazomethane (**2c**) (minor route), whereas loss of N_2 yields selenobenzophenone (**1c**) (major route), which combine to afford the 1,3,4-selenadiazoline **3c** by 1,3-dipolar cycloaddition, both generated in situ, as shown in Scheme 8. Loss of nitrogen and selenium precipitation (twofold loss) gives tetraphenylethylene (**5h**).



Scheme 8

At room temperature, azines **9** might be produced by oxidation of **3** in the presence of a small amount of oxygen in the solvent.

To confirm the formation of intermediates **3**, the reaction of benzophenone hydrazone (**4a**) and 4,4′-dimethoxybenzophenone hydrazone (**4c**) with diselenium dibromide in refluxing dichloromethane was carried out. The obtained products were the symmetrical olefins **5b** and **5h** and the unsymmetrical olefin **5g** in 32, 22, and 32% yields, respectively (Scheme 9). This result is similar to that of the reaction of isolated **1a** with **2c**.



Scheme 9

This method has advantages over other methods. Only two-step reactions are required from commercially available benzophenones. Additionally, ketone hydrazones and diselenium dibromide are stable compounds, with long storage lives. If unsymmetrical tetraarylethylenes are required, the reaction of two different ketone hydrazones with diselenium dibromide will afford the desired unsymmetrical tetraarylethylenes along with symmetrical tetraarylethylenes.

In conclusion, the reaction of selenobenzophenones with diazoalkanes gave the corresponding olefins, which were produced by retrocyclization of 1,3,4-selendiazoline intermediates **3**. Symmetrical tetraarylethylenes were obtained from diaryl ketone hydrazones with diselenium dibromide in the presence of triethylamine, intermediates of which found to be selenobenzophenones **1** and diaryldiazomethanes **2**.

Experimental Section

General: All reactions were carried out under nitrogen. Melting points are uncorrected. 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 (^1H at 400 MHz; ^{13}C at 100 MHz) were recorded in $CDCl_3$ solvent, and chemical shifts are expressed in ppm relative to internal TMS.

Reagents: (Trimethylsilyl)diazomethane was purchased from TCI. 4,4′-Dimethoxyselenobenzophenone (**1a**) and 4,4′-dimethylselenobenzophenone (**1b**) were obtained by the reaction of diarylmethylenetriphenylphosphoranes with elemental selenium.[19] The selenoketone **1c** and diaryldiazomethanes **2c**−**e** were prepared by the method described in the literature.[3b]

Reaction of 4,4′-Dimethoxyselenobenzophenone (1a) with Diazomethane (2a): A solution of **2a** (0.6 mmol) in diethyl ether was added to a solution of **1a** (61 mg, 0.20 mmol) in benzene (5 mL) at room temperature. The mixture was stirred for 30 min, nitrogen gas was evolved and elemental selenium was precipitated. The solution was filtered and the solvents evaporated to give a pale-yellow oil, which was chromatographed over silica gel by elution from hexane/dichloromethane (2:1) to afford 1,1-bis(4-methoxyphenyl)ethylene (**5a**) (24 mg, 0.10 mmol) and tetrakis(4-methoxyphenyl)ethylene (**5b**) (4 mg, 0.009 mmol). **5a:** Colorless crystals, m.p. 144−145 °C (ref.[20] m.p. 143 °C). ^1H NMR ($CDCl_3$): δ = 3.83 (s, 6 H, OMe), 5.29 (s, 2 H, CH_2=), 6.86 (d, 4 H, Ar), 7.28 (d, 4 H, Ar) ppm. ^{13}C NMR ($CDCl_3$): δ = 55.29 (OMe), 116.66 (CH_2=), 123.64 (Ar), 129.41 (Ar), 134.30 (Ar), 148.96 (C=), 159.28 (Ar) ppm. **5b:** Colorless crystals, m.p. 180−180.5 °C, (ref.[21] m.p. 182−183 °C).

Reaction of 4,4′-dimethylselenobenzophenone (**1b**) (38 mg, 0.139 mmol) in benzene with **2a** (3 equiv. in ether) was also carried out, yielding 1,1-bis(4-methylphenyl)ethylene (**5d**) and tetrakis(4-methylphenyl)ethylene (**5e**). **5d:** Pale-orange crystals, 7 mg, 0.034 mmol), m.p. 57−59 °C (ref.[22] m.p. 61 °C). ^1H NMR ($CDCl_3$): δ = 2.35 (s, 6 H, Me), 5.37 (s, 2 H, =CH_2), 7.12 (d, 4 H, Ar), 7.23 (d, 4 H, Ar) ppm. ^{13}C NMR ($CDCl_3$): δ = 21.16 (Me), 112.97 (=CH_2), 128.18, 128.82, 137.40, 138.81, 149.76 ppm. **5e:** Colorless crystals, m.p. 149−150 °C (ref.[21] m.p. 151 °C).

Reaction of 1a with Trimethylsilyldiazomethane (2b): A solution of **2b** (0.6 mL, 10% solution in hexane) was added in one portion to a solution of **1a** (101 mg, 0.33 mmol) in benzene (5 mL) at room temperature. The mixture was stirred for 30 min, nitrogen gas was evolved and elemental selenium was precipitated. The solution was filtered and the solvents evaporated to give pale-yellow oily crystals,

which were chromatographed over silica gel by elution from hexane/dichloromethane (2:1) to afford 2,2-bis(4-methoxyphenyl)-1-trimethylsilylethylene (**5c**) (64 mg, 0.20 mmol) and **5b** (40 mg, 0.087 mmol). **5c:** Colorless oil. (ref.[23] colorless oil). ^{1}H NMR ($CDCl_3$): δ = −0.11 (s, 9 H, Me_3Si), 3.79 (s, 3 H, OMe), 3.84 (s, 3 H, OMe), 6.12 (s, 1 H, CH=), 6.79 (d, 2 H, Ar), 6.87 (d, 2 H, Ar), 7.10 (d, 2 H, Ar), 7.20 (d, 2 H, Ar) ppm. ^{13}C NMR ($CDCl_3$): δ = 0.00 (Me_3Si), 55.10 (OMe), 55.14 (OMe), 113.00 (Ar), 113.13(Ar), 127.03 (CH=), 128.35(Ar), 130.67(Ar), 135.15(Ar), 136.25 (Ar), 156.09(Ar), 158.81(Ar), 159.11 (Ar) ppm. Reaction of **1b** (128 mg, 0.47 mmol) with **2b** (0.4 mL, 10% in hexane) was also carried out at room temperature, yielding 2,2-bis(4-methylphenyl)-1-trimethylsilylethylene (**5f**) (12 mg, 0.043 mmol) and **5e** (56 mg, 0.144 mmol). **5e:** Orange oil. ^{1}H NMR ($CDCl_3$): δ = −0.19 (s, 9 H, Me_3Si), 2.25 (s, 3 H, Me), 2.31 (s, 3 H, Me), 6.13 (s, 1 H, CH=), 6.99 (d, 2 H, Ar), 7.01 (d, 2 H, Ar), 7.07 (d, 2 H, Ar), 7.10 (d, 2 H, Ar) ppm. HRMS: found 280.1655, calcd for $C_{19}H_{24}Si$ [M^+]; 280.1647.

Reaction of 1a with 4,4′-Ditolyldiazomethane (2d): A solution of **2d** (110 mg, 0.50 mmol) in THF (5 mL) was added via a syringe to a solution of **1a** (152 mg, 0.50 mmol) in THF (5 mL) at −78 °C. The reaction mixture was stirred for 1 h, then warmed to room temp. and elemental selenium was precipitated. The resulting solution was filtered and the solvents evaporated to give a pale-orange oil. This was chromatographed over silica gel by elution with hexane/dichloromethane (2:1) to afford 1,1-bis(4-methoxyphenyl)-2,2-bis(4-methylphenyl)ethylene (**5i**) (156 mg, 0.36 mmol), **5b** (5 mg, 0.01 mmol) and **5e** (19 mg, 0.05 mmol) in 72, 5 and 20% yields, respectively. **5i:** M.p. 179−180 °C. ^{1}H NMR ($CDCl_3$): δ = 2.25 (s, 3 H, Me), 3.73 (s, 3 H, OMe), 6.63 (d, 4 H, MeO Ar). 6.89 (s, 8 H, Tol Ar), 6.92 (d, 4 H, MeO Ar) ppm. ^{13}C NMR ($CDCl_3$): δ = 21.15 (Me), 55.05 (OMe), 112.70 (Ar), 128.33 (Ar), 130.95 (Ar), 132.50, 135.52, 136.77, 139.09, 141.45, 157.85 ppm. $C_{30}H_{28}O_2$ (420.5): calcd. C 85.68, H 6.71; found C 85.34, H 6.65. Reaction of **1a** (25 mg, 0.082 mmol) with **2c** (16 mg, 0.080 mmol) was also carried out, yielding 1,1-bis(4-methoxypheny)-2,2-diphenylethylene (**5g**) (11 mg, 0.028 mmol) and **5h** (9 mg, 0.027 mmol). **5g:** M.p. 160−161 °C. (ref.[24] m.p. 154−155 °C). ^{1}H NMR ($CDCl_3$): δ = 3.74 (s, 6 H, OMe), 6.63 (d, 4 H, MeO Ar), 6.95 (d, 4 H, MeO Ar), 6.98−7.02 (m, 4 H, Ph), 7.05−7.16 (m, 6 H, Ph) ppm. $C_{28}H_{24}O_2$ (392.5): calcd. C 85.68, H 6.16; found C 85.82, H 6.17.

Reaction of **1a** (70 mg, 0.23 mmol) with **2e** (61 mg, 0.24 mmol) was also carried out at −45 °C. Tetrakis(4-methoxyphenyl)ethylene (**5b**) was obtained. (87 mg, 0.193 mmol), m.p. 180−181 °C.

Reaction of Di-*tert*-butylselenoketone (1d) with Diphenyldiazomethane (2c): A solution of **2c** (0.204 g, 1.05 mmol) in THF (10 mL) was added to a solution of **1d** (0.205 g, 1.0 mmol) in THF (10 mL) at 0 °C. After being stirred for 2 h, the solvent was evaporated to give pale-yellow crystals, which were crystallized from dichloromethane/hexane to afford yellow crystals of 1,3,4-selenadiazoline (**3e**) (0.287 g, 0.72 mmol), m.p. 112−115 °C. (ref.[3b] m.p. 112−118 °C)

Thermolysis of 3e: A solution of **3e** (0.20 g, 0.5 mmol) in benzene (10 mL) was refluxed for 13 h. Elemental selenium was precipitated and filtered off, and the solvents were evaporated to give pale-blue oily crystals, which were chromatographed over silica gel by elution from hexane, hexane/dichloromethane (2:1), and dichloromethane to afford **5h** (0.010 g, 0.030 mmol), 1,1-di-*tert*-butyl-2,2-diphenylethylene (**5j**) (26 mg, 0.08 mmol), **1c** (0.041 g, 0.020 mmol), and benzophenone (**7a**) (50 mg, 0.275 mmol). **5j:** Colorless crystals, m.p. 138−140 °C (ref.[25] m.p. 140.5−141 °C).

Reaction of 1,3,4-Selenadiazoline 3e with 2,3-Dimethyl-1,3-butadiene: 2,3-Dimethyl-1,3-butadiene (82 mg, 1.0 mmol) in THF (5 mL) was added in one portion to a solution of **3e** (80 mg, 0.2 mmol) in THF (5 mL) at room temp. The resulting solution was refluxed for 6 h, and the solvents evaporated to give pale-yellow oily crystals, which were chromatographed over silica gel by elution with hexane and hexane/dichloromethane (1:1) to afford 4,5-dimethyl-2,2-diphenyl-3,6-dihydro-2*H*-selenopyran (**8**) (40 mg, 0.124 mmol). **8:** Pale-yellow oil (ref.[26] pale-yellow oil).

Reaction of Benzophenone Hydrazone (4a) with Diselenium Dibromide: A solution of diselenium dibromide (640 mg, 2.0 mmol) in dichloromethane (10 mL) was added to a solution of **4a** (196 mg, 1.0 mmol) and triethylamine (410 mg, 4.0 mmol) in dichloromethane (10 mL) at room temperature. The reaction mixture was stirred for 3 h, then poured into water, filtered and extracted with dichloromethane (3 × 5 mL). The combined extract was dried with magnesium sulfate and the solvents evaporated to afford a brown oil, which was chromatographed over silica gel by elution with hexane/dichloromethane (1:1) to afford **5h** (123 mg, 0.37 mmol) and **9a** (2 mg, 0.01 mmol).

The reaction of 4,4′-dimethylbenzophenone hydrazone (**4b**) (224 mg, 1.0 mmol) with diselenium dibromide (640 mg, 2.0 mmol) in the presence of triethylamine (410 mg, 4.02 mmol) was carried out in a similar manner. Olefin **5e** (85 mg, 0.22 mmol) and **9b** (72 mg, 0.17 mmol) were obtained.

Reaction of Benzophenone Hydrazone (4a) with Diselenium Dibromide in Refluxing Benzene: A solution of diselenium dibromide (640 mg, 2.0 mmol) in benzene (10 mL) was added to a refluxing solution of **4a** (196 mg, 1.0 mmol) and triethylamine (410 mg, 4.0 mmol) in benzene (10 mL). After refluxing for 3 h, the reaction mixture was poured into water, filtered and extracted with dichloromethane (3 × 5 mL). The combined extract was dried with magnesium sulfate and the solvents evaporated to afford a brown oil which was chromatographed over silica gel by elution with hexane/dichloromethane (1:1) to afford **5h** (143 mg, 0.43 mmol).

The reaction of 4,4′-dimethylbenzophenone hydrazone (**4b**) (224 mg, 1.0 mmol) with diselenium dibromide (640 mg, 2.0 mmol) in the presence of triethylamine (410 mg, 4.0 mmol) was carried out in a similar manner. Olefin **5e** (159 mg, 0.41 mmol) was obtained.

The reaction of 4,4′-dimethoxybenzophenone hydrazone (**4c**) (256 mg, 1.0 mmol) with diselenium dibromide (640 mg, 2.0 mmol) in the presence of triethylamine (410 mg, 4.02 mmol) was carried out in a similar manner. Olefin **5b** (149 mg, 0.33 mmol) was obtained.

The reaction of 4,4′-dichlorobenzophenone hydrazone (**4c**) (265 mg, 1.0 mmol) with diselenium dibromide (640 mg, 2.0 mmol) in the presence of triethylamine (410 mg, 4.02 mmol) was carried out in a similar manner. Tetrakis(4-chlorophenyl)ethylene (**5k**) (236 mg, 0.42 mmol) was obtained. **5k**: colorless crystals, m.p. 216−217 °C (ref.[14] m.p. 216−217 °C).

Reaction of Diselenium Dibromide with 4a and 4c: A solution of diselenium dibromide (1.28 mg, 4.0 mmol) in dichloromethane (20 mL) was added dropwise to a solution of **4a** (200 mg, 1.02 mmol), **4c** (256 mg, 1.0 mmol), and triethylamine (404 mg, 4.0 mmol) in dichloromethane (15 mL) at room temperature. The reaction mixture was stirred for 5 h, then washed with water (3 × 10 mL), dried with magnesium sulfate, filtered and the solvents evaporated to give pale-brown oily crystals, which were chromatographed over silica gel by elution with hexane and dichloromethane to afford a mixture of **5b** (72 mg, 0.16 mmol), **5g** (86 mg, 0.22 mmol) and **5h** (53 mg, 0.16 mmol). The mixture was separated by gel HPLC.

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