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FIRST ISOLATION OF *CIS*- AND *TRANS*-1,3,4-SELENADIAZOLINES FROM PIVAROPHENONE HYDRAZONES

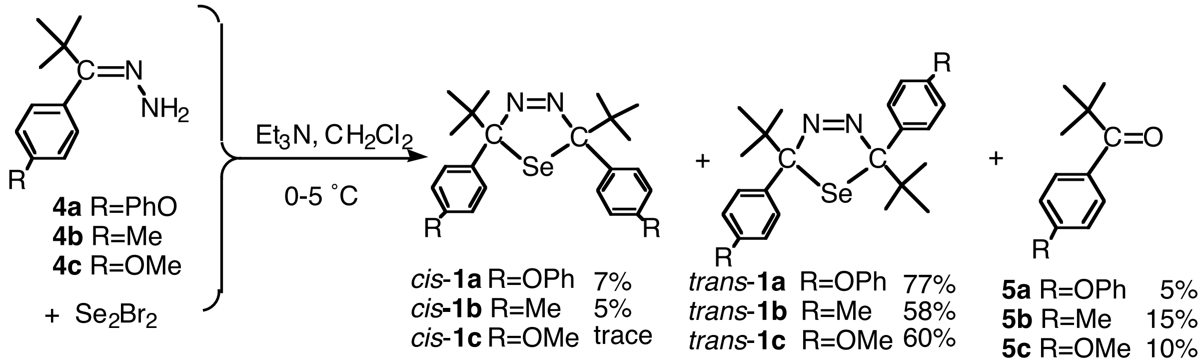
Kentaro Okuma,*,†,‡ Kento Kubo,† and Yoshinobu Yokomori§

†Department of Chemistry, Faculty of Science, Fukuoka University, Jonan-ku, Fukuoka 814-0180, Japan
‡Advanced Materials Institute, Fukuoka University, Jonan-ku, Fukuoka 814-0180, Japan
§Department of Chemistry, National Defense Academy, Hashirimizu, Yokosuka 239-0811, Japan

Abstract – Sterically congested *cis*- and *trans*-1,3,4-selenadiazolines were isolated by one-pot reaction of pivalophenone hydrazones with diselenium dibromide, which suggested *in situ* formation of selenoketone and diazoalkane intermediates. Thermolysis of these compounds gave symmetrical olefins, whereas oxidation afforded the corresponding azines.

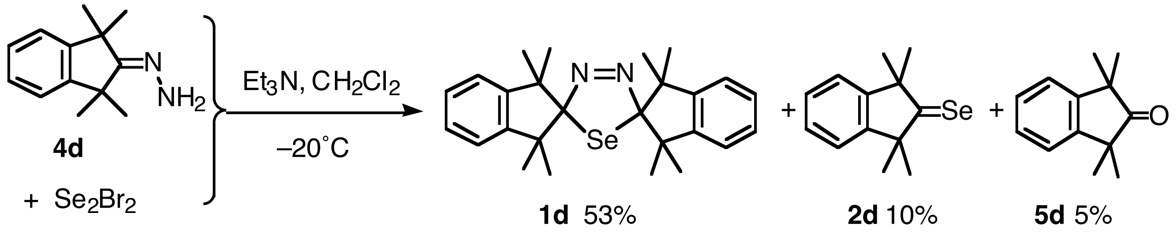
Sterically congested 1,3,4-selenadiazolines (**1**) and 1,3,4-thiadiazolines are interesting compounds for their synthetic application of sterically crowded olefins.[1] It has been reported that the reaction of sterically hindered selenoketones (**2**) with sterically hindered diazoalkanes (**3**) afforded **1**, which decomposed to the corresponding symmetrical olefins *via* thermal two fold extrusion.[1,2] Recently, we have isolated *cis*- and *trans*-1,2,4-trithiolanes from ketones and tetraphosphorus decasulfide.[3] However, there is no report on the isolation of *cis*- and *trans*-1,3,4- selenadiazolines. We report herein the first isolation of *cis*- and *trans*-**1** and one-pot synthesis of **1** from ketone hydrazones (**4**).

Treatment of *p*-phenoxypivalophenone hydrazone (**4a**) with diselenium dibromide in the presence of triethylamine at 0°C resulted in the formation of *cis*-2,5-di-*tert*-butyl-2,5-di-*p*-phenoxyphenyl-1,3,4-selenadiazoline (*cis*-**1a**), *trans*-2,5-di-*tert*-butyl-2,5-di-*p*-phenoxyphenyl-1,3,4-selenadiazoline (*trans*-**1a**), and *p*-phenoxypivalophenone (**5a**) (Scheme 1).[4] The structures of *cis*-**1a** and *trans*-**1a** were confirmed by their ^{1}H NMR spectrum and elemental analysis. The chemical shift of *tert*-butyl group of *trans*-**1a** (0.89 ppm) is higher than that of *cis*-**1a** (1.19 ppm), whereas chemical shifts of aromatic group of *trans*-**1a** (6.91 and 7.01 ppm) are lower than those of *cis*-**1a** (6.57 and 6.80 ppm). This observation suggests that aromatic plane of *cis*-**1a** was on the aromatic plane whereas *tert*-butyl group of *trans*-**1a** was on the aromatic plane.



Scheme 1.

The present result is quite different from Guziec and Okazaki *et al.* Guziec and Moustakis reported the synthesis of 1,1,3,3-tetramethylindane-2-selone (**2d**) by the reaction of 1,1,3,3-tetramethylindane-2-one hydrazone (**4d**) with diselenium dibromide in the presence of triethylamine.[5] Okazaki *et al.* reported the synthesis of **2d** by the reaction of diselenium dichloride with Grignard reagents of the corresponding ketone hydrazones.[6] They did not mention the formation of 1,3,4-selenadiazoline (**1d**). Thus, we then tried the reaction of other ketone hydrazones (**4**) with diselenium dibromide to confirm the formation of **1**. Treatment of **4d** with diselenium dibromide at –20˚C resulted in the formation of **1d** (53%) along with **2d** (10%) and 1,1,3,3-tetramethylindan-2-one (**5d**) (5%) (Scheme 2). When the reaction was carried out at rt, **2d** was obtained in 55 % yield. Thus, temperature plays an important role for the formation of **1d**. Other reactions were carried out in a similar manner (Table 1).

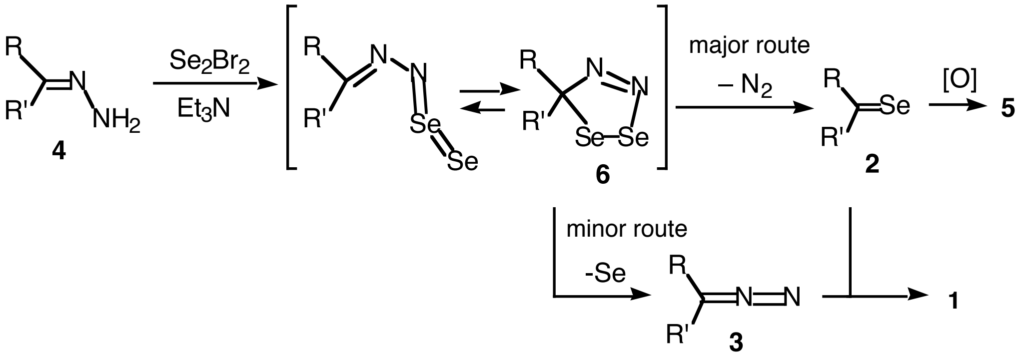


Scheme 2.

Table 1. Reaction of **4** with Diselenium Dibromide

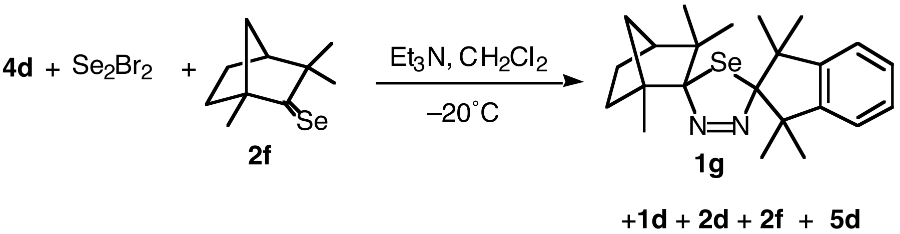
	Ketone Hydrazone	Conditions		Products (Yields/%)			
4		Temperature (˚C)	Time (h)	**1**		**2**	**5**
4d	Tetramethylindanone	– 40	4	**1d**	26	10	1
		– 20	2	**1d**	53	10	5
		0	2	**1d**	3	55	7
		rt	2	**1d**	5	55	9
4e	2,2,5,5-Tetramethylcyclopentanone	– 20	2	**1e**	40	8	25
4f	Fenchone	– 20	2	**1f**	35	15	30

The reaction most likely proceeds as follows. The anion of ketone hydrazone (**4**) reacts with diselenium dibromide to afford 1,2,3,4-diselenadiazoline (**6**). Extrusion of selenium from **6** affords diazoalkane (**3**) (minor route), whereas, N_2 is extruded to afford the selenoketone (**2**) (major route). Selenadiazoline (**1**) is most likely formed by 1,3-dipolar cycloaddition of selenoketone (**2**) with the diazo compound (**3**), both generated in situ, as shown in Scheme 3. The proposed mechanism is similar to that of 1,2,4-telluradiazoline suggested by Okazaki *et al.*[7]



Scheme 3.

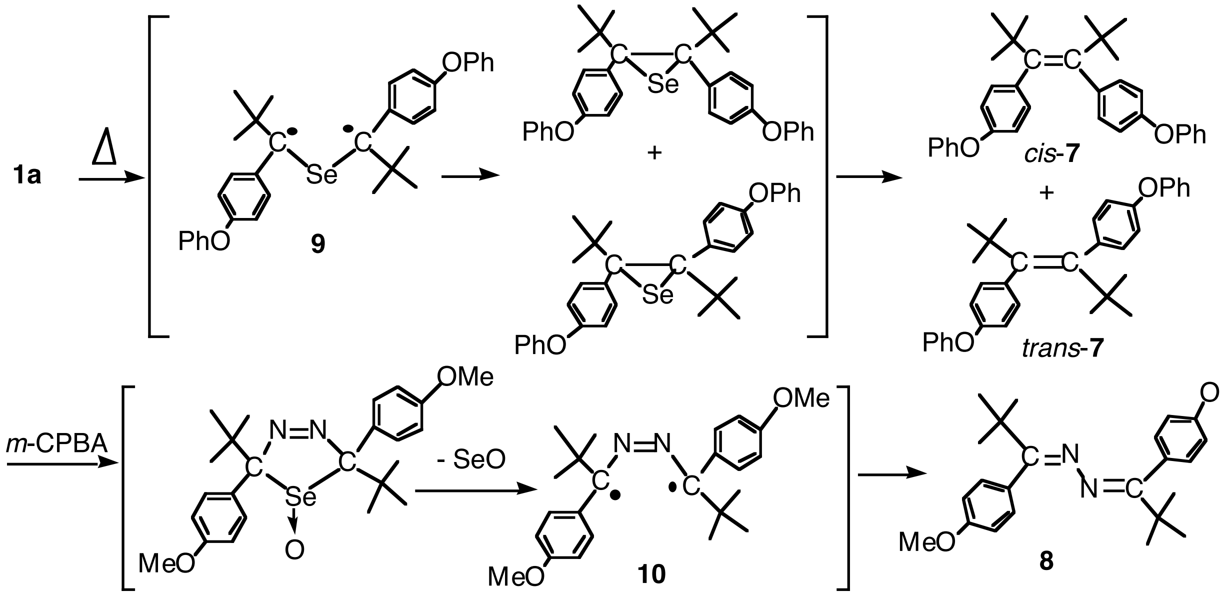
Okazaki *et al.* also suggested the formation of diazoalkane intermediates from ketone hydrazones and diselenium dichloride.[8] Actually, when the reaction of **4d** with diselenium dibromide was carried out in the presence of selenofenchone (**2f**), unsymmetrical selenadiazoline (**1g**) was obtained in 7% along with symmetrical selenadiazoline (**1d**) (25%), suggesting that the intermediates of this reaction should be diazoalkane (**3**) and selenoketone (**2**) (Scheme 4).



Scheme 4.

Since *cis*- and *trans*-1,3,4-selenadiazolines were isolated, we then tried the thermolysis of **1a** to confirm the reaction mechanism of two-fold extrusion. Heating of *trans*-**1a** up to 150°C resulted in the formation of *cis*-olefin (*cis*-**7**, 10%) and *trans*-olefin (*trans*-**7**, 90%), whereas thermolysis of *cis*-**1a** gave the *cis*-**8** (33%) and *trans*-**7** (66%). Oxidation of **1c** with *m*-CPBA at room temperature resulted in the formation of the corresponding azine (**8**, 52%) and pivalophenone **5c** (28%). These results suggested that the reaction might proceed through biradical intermediates. Heating of **1** results into the expulsion of nitrogen gas and biradical (**9**), which recombined to give episelenide. Episelenide is too unstable to isolate, resulting in the formation of *cis*-**7** ant *trans*-**7**. The biradical intermediate equilibrates to more stable conformer, which results in the formation of *trans* isomers. On the other hand, in the case of oxidation, initial fission of carbon-selenium bond results in the formation of biradical (**10**), which easily isomerizes to azine (**8**) (Scheme 5).

In summary, we have isolated *cis*- and *trans*-1,3,4-selenadiazolines. This method provides 1,3,4-selenadiazolines (**1**) in a one-pot operation unlike Barton's method,[1b,1c] which requires isolation of selones and the diazoalkanes. It proved that the only one precursor, ketone hydrazone, provides *in situ* source of sterically hindered **1**, olefins, and azines.



Scheme 5.

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4. Satisfactory elemental analysis and mass spectra were obtained for all the new compounds. *cis*-**1a**: 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, 40.38, 116.63, 118.40, 121.31, 122.89, 129.45, 129.57, 135.67, 155.35, 157.01. *trans*-**1a**: mp 162-163 ˚C. ^{1}H NMR ($CDCl_3$) δ=0.89 (s, 18H, *tert*-Bu), 6.91 (d, 4H, *J*=8 Hz, Ar), 7.01 (d, 4H, *J*=8 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, 41.62, 116.94, 118.91, 123.26, 126.52, 129.52, 129.56, 137.52, 156.05, 156.68.
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