

Generation of 1,3-Chalcogenaza-1,3-butadienes by Thermal Cycloreversion of 2,4,6-Trisubstituted 6*H*-1,3,5-Oxachalcogenazines

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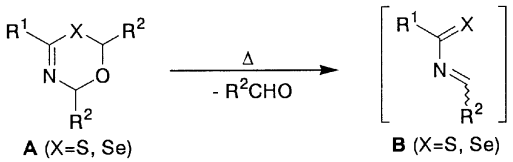
1,3-Thiaza- and 1,3-selenaza-1,3-butadienes bearing several substituents at the C-2 and C-4 positions were generated through thermal cycloreversion of 6*H*-1,3,5-oxathiazines or 6*H*-1,3,5-oxaselenazines, respectively, and the heterodienes were efficiently trapped by using acetylenic dienophiles. When 6*H*-1,3,5-oxathiazines or 6*H*-1,3,5-oxaselenazines were heated in the presence of nucleophiles, such as alcohols or thiols, the corresponding 1,4-adducts of the heterodienes with the nucleophiles were obtained in good yields. On the other hand, heating of 6*H*-1,3,5-oxathiazines or 6*H*-1,3,5-oxaselenazines in the absence of trapping agents afforded several products which originated from the *in situ* generated 1,3-chalcogenaza-1,3-butadienes; also the heterodienes were not isolated or observed directly as the monomeric forms at all.

Recently, interest concerning the generation and trapping of reactive chalcogenocarbonyl compounds has concentrated on an extension to highly reactive analogues possessing higher π-conjugation systems. However, among various aza-1,3-diene derivatives, the generation of 1,3-chalcogenaza-1,3-butadienes **B**(X = S, Se) has less been studied in spite of their synthetic potentiality as novel and versatile building blocks of chalcogen- and nitrogen-containing various heterocycles. Actually, studies on the generation and trapping of 1,3-thiaza- and 1,3-selenaza-1,3-butadienes **B**(X = S, Se) bearing some substituents at the C-2 and C-4 positions have been achieved by several groups.[1–19] However, these studies never resulted in the isolation or detection of the reactive species, except for some electronically-stabilized *N*-thioacyl- and *N*-selenoacylamidine derivatives.[20–34] In most cases, these species were converted into various heterocyclic compounds by [4+2]-type cycloaddition with dienophiles, by [4+2] type dimerization, or by 1,4-addition of H_2S, H_2Se, or their synthetic equivalents.

During our attempts to generate various reactive species bearing a chalcogenocarbonyl functionality by using the ring cleavage of suitable cyclic precursors possessing heteroacetal-type substructures,[35–39] it was strongly expected that heterodienes **B** would be efficiently generated by thermally- or Lewis acid-induced retro-[4+2] type cycloreversion of 6*H*-1,3,5-oxachalcogenazines **A**(X = S, Se), as shown in Scheme 1. According to such an expectation, we previously reported the generation and trapping of 1,3-selenaza-1,3-butadienes **B**(X = Se).[40] In this paper, we would like to give a full account on the generation of heterodienes **B**(X = S, Se) by thermal cycloreversion of **A**(X = S, Se) and trapping of such reactive species by using various dienophiles and nucleophiles. Results concerning attempts to isolate or detect heterodienes **B** are also mentioned in this paper.

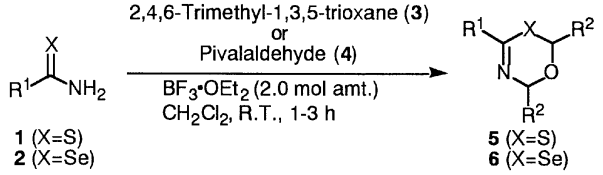


Scheme 1.

Results and Discussion

Preparation of 6*H*-1,3,5-Oxathiazines (5) and 6*H*-1,3,5-Oxaselenazines (6). 6*H*-1,3,5-Oxathiazines **5** and 6*H*-1,3,5-oxaselenazines **6** bearing substituents at the C-2, C-4, and C-6 positions were at first prepared by treating a dichloromethane solution of arenecarbochalcogenoamides (**1**, **2**), such as thiobenzamide (**1a**),[41,42] *p*-chlorobenzothioamide (**1c**),[41] selenobenzamide (**2a**),[43] or *p*-chlorobenzoselenoamide (**2c**),[43] with 2,4,6-trimethyl-1,3,5-trioxane (paraldehyde, **3**) or pivalaldehyde (**4**) and $Et_2O{\cdot}BF_3$ at room temperature according to reported methods.[7,44] In all cases, the physical data of the products, including the MS, IR, ^{1}H NMR, and ^{13}C NMR spectra, were fully consistent with the structures of **5a–d** and **6a–d**. Especially, the physical data of **6a** and **6b** were identical in all respects with those of the reported data.[44] The relative stereochemistry of these products was confirmed to be *cis* in all cases by NMR measurements based on the NOE experiments.[44] All results concerning the preparation of **5a–d** and **6a–d** are given in Table 1. However, a similar treatment of a dichloromethane solution of selenobenzamide (**2a**) with benzaldehyde and $Et_2O{\cdot}BF_3$ only afforded the recovery of substrates,

Table 1. Preparation of 6*H*-1,3,5-Oxathiazines **5** and 6*H*-1,3,5-Oxaselenazines **6**



Substrate			Reagent (**3**, **4**)	Product[a]		Yield
R^1	X	**1**, **2**	(mol amt.)	R^2	**5**, **6**	/%
C_6H_5	S	**1a**	**3** (0.8)	CH_3	**5a**	95
C_6H_5	S	**1a**	**4** (2.4)	t-C_4H_9	**5b**	43
p-ClC_6H_4	S	**1c**	**3** (0.8)	CH_3	**5c**	38
p-ClC_6H_4	S	**1c**	**4** (2.4)	t-C_4H_9	**5d**	32
C_6H_5	Se	**2a**	**3** (0.8)	CH_3	**6a**	56
C_6H_5	Se	**2a**	**4** (2.4)	t-C_4H_9	**6b**	32
p-ClC_6H_4	Se	**2c**	**3** (0.8)	CH_3	**6c**	53
p-ClC_6H_4	Se	**2c**	**4** (2.4)	t-C_4H_9	**6d**	44

a) Single stereoisomers. The relative stereochemistry of the products was determined to be *cis* by NOE experiments between the C-4 and C-6 protons of **5a** and **6a**.

and attempts starting from selenoacetamide or propaneselenoamide and 2,4,6-trimethyl-1,3,5-trioxane (**3**) in a similar manner only gave complicated results; further, the preparation of the target compounds **6** bearing an alkyl substituent at the C-2 position was not successful at all.

Heating of 6*H*-1,3,5-Oxathiazines (5) or 6*H*-1,3,5-Oxaselenazines (6) in the Presence of an Acetylenic Dienophile, *p*-Benzoquinone, or Diethyl Azodicarboxylate (DEAD). A benzene or a toluene solution of 6*H*-1,3,5-oxathiazines **5** or 6*H*-1,3,5-oxaselenazines **6** was treated with a 10 molar amount of dimethyl acetylenedicarboxylate (DMAD), and the reaction mixture was heated for several hours at refluxing temperature under an Ar atmosphere. The crude reaction mixture was subjected to chromatographic separation to obtain 4*H*-1,3-thiazine **9** or 4*H*-1,3-selenazines **11** as the cycloadducts of 1,3-thiaza-1,3-butadienes **7** or 1,3-selenaza-1,3-butadienes **8** in high yields. Furthermore, the treatment of **5a**, **6a**, or **6c** with methyl propiolate in a similar manner also afforded the corresponding cycloadducts **10a**, **12a**, or **12c**, respectively, as sole regioisomers. The ^{1}H NMR spectra of **10a**, **12a**, and **12c** revealed long-range coupling between the methine protons at the C-4 position and the vinyl protons at the C-6 position of these compounds with small coupling constants (**10a**: J = ~0 Hz, **12a**: J = ~1.5 Hz, **12c**: J = ~0 Hz). The NMR experiments of these compounds also revealed no NOE between the methine protons and the vinyl protons of these products. These results clearly showed that the methoxycarbonyl group of **10a**, **12a**, or **12c** was located at the C-5 position.

The formation of cycloadducts of these heterodienes, **7** and **8** (Chart 1), with highly reactive acetylenic dienophiles must be explained by the usual [4+2]-type cycloaddition, including the reaction of heterodienes (**7**, **8**) as novel 4π systems. The regioselectivity of the cycloaddition of the heterodienes with methyl propiolate was also fully consistent with the expectation from FMO theory that predicted the favored orbital interactions between the HOMO of the heterodienes and the LUMO of methyl propiolate. However, an alternative ionic stepwise mechanism including the nucleophilic attack of the sulfur or selenium atom of the heterodienes to the dienophiles followed by the ring-closure remained as a possible route to afford these [4+2]-type cycloadducts.

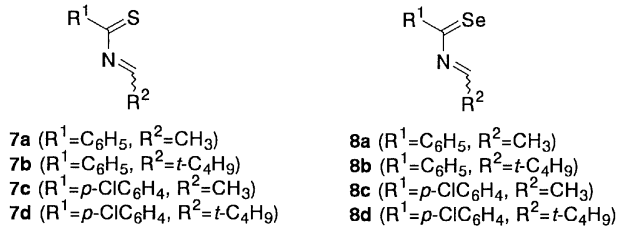
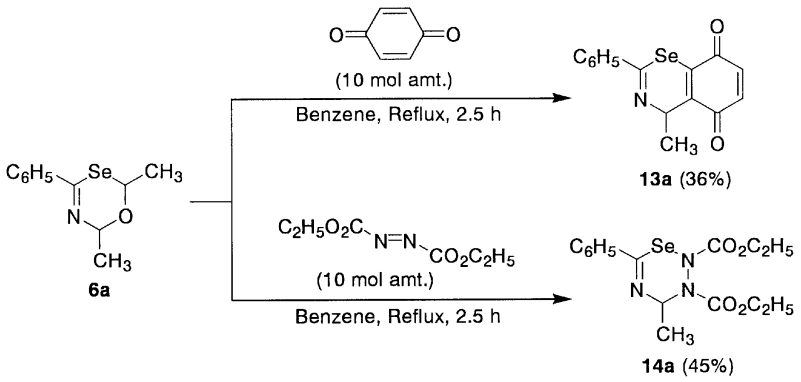


Chart 1. Structures of 1,3-Chalcogenaza-1,3-butadienes **7** and **8**.

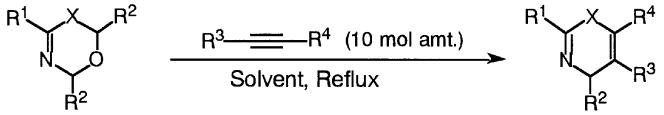
A similar treatment of **6a** with *p*-benzoquinone or diethyl azodicarboxylate (DEAD) also afforded **13a** or **14a**, respectively, in modest yields. It was naturally assumed that **13a** was afforded by cycloaddition of the *in situ* generated 1,3-selenaza-1,3-butadiene **8a** with *p*-benzoquinone, followed by dehydrogenation through aerobic oxidation during the usual workup (Scheme 2). Burger has already reported on the cycloaddition of 4-trifluoromethyl-1,3-thiaza-1,3-butadiene with the cyano group of TCNE.[13] However, in our case, the treatment of **6a** with TCNE only gave a complex mixture. All results concerning the reactions are given in Table 2.

Heating of 6*H*-1,3,5-Oxathiazines (5) or 6*H*-1,3,5-Oxase-



Scheme 2.

Table 2. Heating of 6*H*-1,3,5-Oxathiazines **5** or 6*H*-1,3,5-Oxaselenazines **6** in the Presence of Acetylenic Dienophiles



5 (X=S)
6 (X=Se)

9, **10** (X=S)
11, **12** (X=Se)

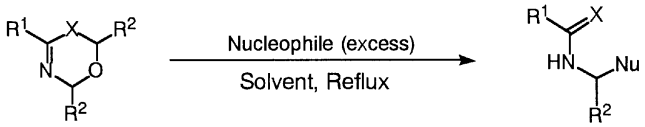
Substrate				Dienophile		Solvent	Time	Product	Yield[a]
R^1	R^2	X	**5**, **6**	R^3	R^4		/h	**9–12**	/%
C_6H_5	CH_3	S	**5a**	CO_2Me	CO_2Me	Toluene	1	**9a**	85
C_6H_5	*t*-C_4H_9	S	**5b**	CO_2Me	CO_2Me	Toluene	4	**9b**	71
C_6H_5	CH_3	S	**5a**	CO_2Me	H	Toluene	3	**10a**	42
C_6H_5	CH_3	Se	**6a**	CO_2Me	CO_2Me	Benzene	2.5	**11a**	78
C_6H_5	*t*-C_4H_9	Se	**6b**	CO_2Me	CO_2Me	Benzene	2.5	**11b**[b]	53
p-ClC_6H_4	CH_3	Se	**6c**	CO_2Me	CO_2Me	Benzene	2.5	**11c**	46
C_6H_5	CH_3	Se	**6a**	CO_2Me	H	Benzene	2.5	**12a**[c]	76
p-ClC_6H_4	CH_3	Se	**6c**	CO_2Me	H	Benzene	2.5	**12c**[c]	33

a) Isolated yields. b) Obtained as a conjugated enolic form. c) Single regioisomer.

lenazines (6) in the Presence of a Nucleophilic Reagent. Heating an ethanolic solution of 6*H*-1,3,5-oxathiazine **5a** at refluxing temperature for a prolonged time afforded the recovery of **5a**. However, a similar heating of a toluene solution of **5a** in the presence of a 10 molar amount of ethanol or 2-propanol at refluxing temperature gave **15a** or **15b**, respectively, in high yields. On the other hand, when 6*H*-1,3,5-oxaselenazines **6** were heated in a methanolic or an ethanolic media under an Ar atmosphere, the 1,4-adducts (**17**, **18**) of 1,3-selenaza-1,3-butadienes **8** with the alcohols were obtained in good yields in all cases. These results indicated that a higher reaction temperature was required for the thermal cycloreversion of 6*H*-1,3,5-oxathiazines **5** than those cases starting from the selenium analogues **6**. The treatment of a benzene solution of **6a** with a 10 molar amount of benzenethiol or phenylmethanethiol at refluxing temperature also gave the corresponding 1,4-adducts, **19a** or **20a**, respectively, in good yields. All results of the reactions are given in Table 3.

In contrast, the treatment of a benzene solution of **6a** with a 10 molar amount of propylamine in a similar manner at refluxing temperature only afforded *N*-propylselenobenzamide in 56% yield, and a treatment of **6b** with propylamine, even at room temperature, also gave a similar result. It was supposed that *N*-propylselenobenzamide was given through a route including the formation of heterodiene **8a** followed by nucleophilic 1,4-addition of propylamine to **8a**, an intramolecular nu-

Table 3. Heating of 6*H*-1,3,5-Oxathiazines **5** or 6*H*-1,3,5-oxaselenazines **6** in the Presence of Nucleophilic Reagents



5 (X=S)
6 (X=Se)

15, **16** (X=S)
17-**20** (X=Se)

Substrate				Nucleophile	Solvent	Time	Product	Yield[a]
R^1	R^2	X	**5**, **6**	/Nu–H (excess)		/h	**15–20**	/%
C_6H_5	CH_3	S	**5a**	C_2H_5OH	C_2H_5OH	4	**15a**[b]	0
C_6H_5	*t*-C_4H_9	S	**5b**	C_2H_5OH[c]	Toluene	4	**15b**	99
C_6H_5	CH_3	S	**5a**	*i*-C_3H_7OH[c]	Toluene	4	**16a**	95
C_6H_5	CH_3	Se	**6a**	CH_3OH	CH_3OH	4	**17a**	62
C_6H_5	CH_3	Se	**6a**	C_2H_5OH	C_2H_5OH	4	**18a**	66
C_6H_5	*t*-C_4H_9	Se	**6b**	C_2H_5OH	C_2H_5OH	4	**18b**	53
p-ClC_6H_4	CH_3	Se	**6c**	CH_3OH	CH_3OH	4	**17c**	92
p-ClC_6H_4	CH_3	Se	**6c**	C_2H_5OH	C_2H_5OH	4	**18c**	85
C_6H_5	CH_3	Se	**6a**	C_6H_5SH[c]	Benzene	4	**19a**	85
C_6H_5	CH_3	Se	**6a**	$C_6H_5CH_2SH$[c]	Benzene	4	**20a**	82
C_6H_5	CH_3	Se	**6a**	$C_3H_7NH_2$[d]	Benzene	4	—	0[e]

a) Isolated yields. b) **5a** was recovered in quantitative yield. c) 10 Molar amount of alcohol or thiol was treated for the reactions. d) 10 Molar amount of propylamine was treated with **6a** for the reaction. e) *N*-Propylbenzenecarboselenoamide was obtained in 56% yield.

cleophilic attack of the nitrogen atom of the newly-introduced propylamino group to the C-2 carbon of the 1,4-adduct, and a final elimination of aldimine from the intermediate.

Heating of 6*H*-1,3,5-Oxathiazine (5) in the Absence of Trapping Agents. Heating of a toluene solution of **5a** or **5c** at refluxing temperature mainly afforded four products (5,6-dihydro-4*H*-1,3,5-thiadiazines **21**, 5,6-dihydro-4*H*-1,3-thiazines **22**, 3*H*-1,2,4-dithiazoles **23**) and the starting arenecarbothioamides **1** in all cases.

The structures of **21a** and **21c** were determined to be inseparable epimeric mixtures of the [4+2]-type dimers (major-**21a**:minor-**21a** = 4:1, major-**21c**:minor-**21c** = 2:1) of 1,3-thiaza-1,3-butadienes (**7a**, **7c**) from their spectral data.[12] The ^{1}H NMR and ^{13}C NMR spectra of **21a** and **21c** measured in $CDCl_3$ at 27 °C showed rather complicated patterns with the broadening signals. However, the ^{1}H NMR spectra of **21a** measured at –30 °C revealed sharpened and simplified signal patterns including the pairs of doublets of the methyl groups of the C-4 and the C-6 positions of **21a** at δ = 1.77 and 1.98 ppm for the major isomer and at δ = 1.71 and 1.90 ppm for the minor isomer, respectively. The pairs of quartets of the methine protons of the C-4 and the C-6 positions of **21a** in the ^{1}H NMR spectra of **21a** were also observed at δ = 5.60 and 7.08 ppm for the major isomer and at δ = 5.88 and 7.35 ppm for the minor isomer, respectively. The ^{13}C NMR spectra of **21a** measured at –30 °C showed a couple of thiocarbonyl carbon signals at δ = 198.2 and 201.3 ppm along with the doublet signals at δ = 52.9, 70.0, and 71.1 ppm, assigned to the methine carbons at the C-4 and the C-6 positions of the major and minor isomers of **21a**, respectively. The ^{13}C NMR spectrum of **21c** measured at –30 °C also showed similar spectral features to those of **21a**. It was strongly suggested that the temperature-dependent spectral patterns of **21** in ^{1}H NMR and ^{13}C NMR spectra showed a conformational change of the **21**, including a rotation of the C-N bond of the thioamide moiety at above –30 °C. However, the major conformation of **21** at low temperature was not clarified from these spectral data.

The physical data including MS, IR, ^{1}H NMR, and ^{13}C NMR spectra also showed that both **22a** and **22c** were inseparable epimeric mixtures (about 1:1 in both cases) of the [4+2]-type dimers of 1,3-thiaza-1,3-butadienes, **7a** or **7c**, with *N*-vinylthioamides, **25a** or **25c**, which were assumed to be formed through the double-bond isomerization of **7a** or **7c**, respectively.[16,30] Compounds **22** were assumed to be afforded through the 1,4-addition of **25** to the C-3 positions of heterodienes **7** (Table 4).

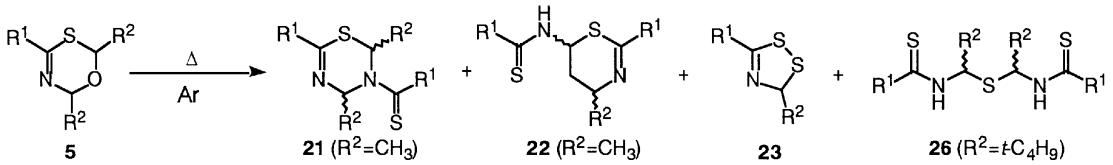
On the other hand, heating of a toluene solution of **5b** bearing a *t*-butyl group at the C-4 position at refluxing temperature in a similar manner gave a diastereomeric mixture of **26b** (about 5:3 ratio estimated by the integration of their ^{1}H NMR spectra for each case) and **23b** along with unidentified several products; neither the dimeric products nor the monomeric heterodiene **7b** were not found at all in the reaction mixture.

The formation of thioamides **1** during a thermal reaction might be explained by a hydrolytic cleavage of the starting materials **5** or heterodienes **7** caused by a trace amount of water contained in the solvent or in the atmosphere or the solvent.

Heating of 6*H*-1,3,5-Oxathiazine (5) in the Presence of a Thioamide. When a toluene solution of 6*H*-1,3,5-oxathiazine **5a** was treated with 1.0 molar amount of thiobenzamide (**1a**) at refluxing temperature for 5 h, 6*H*-1,3,5-thiadiazine **24a** was obtained in low yields along with an inseparable epimeric mixture of 4*H*-1,3-thiazines **22a**; the treatment of a toluene solution of **5a** with thiobenzamide (**1a**) in the presence of 1.0 molar amount of $Et_2O{\cdot}BF_3$ at refluxing temperature also gave the same products in a similar product-composition. A similar heating of **5b** in the presence of **1a** gave 3*H*-1,2,4-dithiazoles **23** and an epimeric mixture of **26** in low yields; also actually, heating a toluene solution of **5b** in the presence of an excess amount of thioacetamide at refluxing temperature for 3 h gave **26b** (49%, major-**26b**:minor-**26b** = 5:3) and **23b** (14%) in much higher yields (Table 5). This result strongly suggests that both **26b** and **23b** were formed by the reaction of heterodienes **7b** with thioamides. Thioacetamide has been widely regarded and used as a sulfur nucleophile, which is a stable synthetic equivalent of H_2S.[45] Thus, the formation mechanisms of all products by the heating of **5** in the presence of thioamides were explained by the nucleophilic 1,4-addition of heterodienes **7** with *in situ* generated thiobenzamide (**1a**) followed by a thermal elimination of benzonitrile from the adducts to form intermediary thiol species, which might give **22** and **23** through a further 1,4-addition of heterodienes **7** or through aerobic oxidation, respectively.

Generation of 1,3-Thiaza-1,3-butadienes (7a) by Ther-

Table 4. Thermal Reaction of 6*H*-1,3,5-Oxathiazines **5**

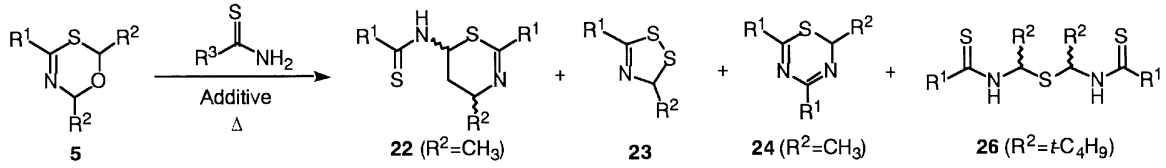


5 **21** (R^2=CH_3) **22** (R^2=CH_3) **23** **26** (R^2=*t*-C_4H_9)

Substrate			Solvent	Temp	Time	Yields/%[a]			
R^1	R^2	**5**			/h	**21** (major : minor)[b]	**22** (isomeric ratio)[b]	**23**	**26**
C_6H_5	CH_3	**5a**	Toluene	Reflux	3	73 (**21a**, 4 : 1)	22 (**22a**, 1 : 1)	trace (**23a**)	0 (**26a**)
C_6H_5	*t*-C_4H_9	**5b**	Toluene	Reflux	5	0	—	trace (**23b**)	trace (**26b**)[c]
p-ClC_6H_4	CH_3	**5c**	Toluene	Reflux	5	49 (**21c**, 4 : 1)	19 (**22c**, 1 : 1)	trace (**23c**)	0 (**26c**)

a) Isolated yields. b) Estimated by integration of the ^{1}H NMR spectrum. c) The ratio of major-**26b** : minor-**26b** was estimated to be 5 : 3 by integration of the ^{1}H NMR spectrum of the diastereomeric mixture.

Table 5. Thermal Reaction of 6*H*-1,3,5-Oxathiazines **5** in the Presence of Thioamide



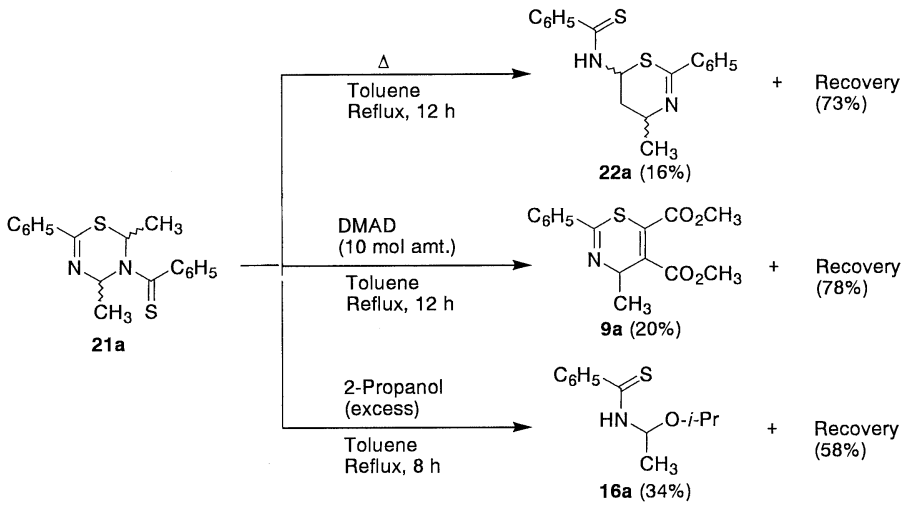
Substrate			Thioamide	Additive	Solvent	Temp	Time	Yields/%[a]			
R^1	R^2	**5**	R^3	(mol amt.)			/h	**22** (isomeric ratio)[b]	**23**	**24**	**26**
C_6H_5	CH_3	**5a**	C_6H_5	—	Toluene	Reflux	5	22 (**22a**, 1 : 1)	trace (**23a**)	11 (**24a**)	0
C_6H_5	CH_3	**5a**	C_6H_5	BF_3·OEt_2 (1.0)	Toluene	Reflux	5	44 (**22a**, 1 : 1)	17 (**23a**)	5 (**24a**)	0
C_6H_5	t-C_4H_9	**5b**	C_6H_5	—	Toluene	Reflux	9	—	22 (**23b**)	0 (**24b**)	trace (**26b**)
C_6H_5	t-C_4H_9	**5b**	CH_3	—	Toluene	Reflux	3	—	14 (**23b**)	0 (**24b**)	49 (**26b**)[c]

a) Isolated yields. b) Estimated by integration of the ^{1}H NMR spectrum. c) The ratio of major-**26b** : minor-**26b** was estimated to be 5 : 3 by integration of the ^{1}H NMR spectrum of the diastereomeric mixture.

mal Cycloreversion of 2*H*-1,3,5-Thiadiazines (21). When a toluene solution of cycloadduct **21a** was heated at refluxing temperature for 12 h, only a small amount of epimeric mixture of **22a** (16% combined yield) was afforded along with the recovery of **21a** (73%). Heating a toluene solution of **21a** in the presence of 10 molar amount of DMAD at refluxing temperature for 12 h afforded the cycloadduct **9a** in only 20% yield along with the recovery of **21a** (78%); a similar heating of **21a** in 2-propanol at refluxing temperature for 8 h also gave the corresponding 1,4-adduct **16a** in 34% yield along with the recovery of **21a** (58%), as shown in Scheme 3. These results indicated that **21** should be recognized as new stable precursors of 1,3-thiaza-1,3-butadienes **7** and that the retro [4+2]-type thermal cycloreversion of **21** requires a higher temperature than the thermal cycloreversion of **5** mentioned above.

Thermal Reaction of 6*H*-1,3,5-Oxaselenazines (6) in the Absence of Trapping Agents or in the Presence of a Dienophile. Heating of a benzene solution of 6*H*-1,3,5-oxaselenazines **6** at refluxing temperature under an Ar atmosphere in the absence of trapping agents gave different results from those of the thermal reaction of 6*H*-1,3,5-oxathiadines **5**; in all cases 6*H*-1,3,5-selenadiazines **27**, 3*H*-1,2,4-diselenazoles **28**, an epimeric mixture of 2*H*-1,3-imidazolines **29**, and unexpected selenoamides **30** were obtained as the products. Even if **6** was subjected to heating in the presence of an excess amount of reactive dienophiles, such as cyclohexene, phenylacetylene, maleic anhydride, or *p*-tolunitrile, the same products (**27**, **28**, **29**, and **30**) in all cases were obtained in similar ratios to those obtained from the reaction in the absence of trapping agents. Actually, the expected 1,3-selenaza-1,3-butadienes **8** were not found or detected at all as monomeric forms in the reaction mixture, and the expected dimeric products **32** were not found in the crude reaction mixture. On the other hand, heating a benzene solution of **6a** in a similar manner in the presence of a 2 molar amount of Et_2O·BF_3 only caused ring cleavage to give selenobenzamide **2a** in modest yield through the reverse-reaction of formation of **6a**. Thus, it was clear that Lewis acids promoted the hydrolytic ring cleavage of the cyclic chalcogenoaminoacetal- and chalcogenoimidate-moieties of **6a**.

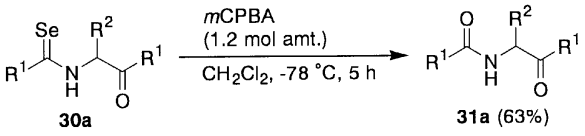
The structures of products **28** were confirmed by their physical data, including the MS, IR, ^{1}H NMR, and ^{13}C NMR spectra, and their elemental analysis data were also consistent with their structures. Especially, the ^{1}H NMR and ^{13}C NMR spectral patterns of **28** were similar to those of the sulfur analogues and the reported selenium derivatives. It was naturally supposed that **28** were originated from 1,4-addition of the *in situ* generat-



Scheme 3.

ed selenoamides to the C-4 position of 1,3-selenaza-1,3-butadienes **8** followed by the extrusion of arylonitriles and aerobic oxidation of the resulting adducts according to the analogous formation of **23** from **5** in the sulfur series.

On the other hand, the spectral data showed that the ring system of **29** was different from that of the [4+2]-type dimers (**21**), which were obtained by thermal reaction of **5** in the sulfur series. The mass spectra of **29** in each cases revealed the typical set of parent ion peaks with a significant isotope distribution pattern of the molecule containing one selenium atom, and ^{1}H NMR and ^{13}C NMR also showed that **29** were isolated as epimeric mixtures (about 1:1 ratio estimated from the integration of the ^{1}H NMR spectra) possessing one selenocarbonyl functionality. It was strongly suggested that **29** originated from the [4+2]-type dimers of the *in situ* generated 1,3-selenaza-1,3-butadienes **8** as the similar formation route from **7** to **21**. The structures of **30** were determined from their ^{1}H NMR and ^{13}C NMR spectral data and, especially, the structure of **30a** was confirmed by selective conversion into the corresponding amide (2-amino-*N*-benzoylpropiophenone (**31a**))[46–48] in 63% yield by treating with a 1.2 molar amount of *m*CPBA (Scheme 4).[49,50]



Scheme 4.

The structures of **27** were not fully defined only from their spectral data. The elemental-analysis data supported the molecular formula of $C_{16}H_{14}N_2Se$ for **27a**, and three plausible structures, 6*H*-1,3,5-selenadiazine **C**, 4*H*-1,2,5-selenadiazine **D**, and 4*H*-1,3,5-selenadiazine **E**, were proposed for **27a** (Chart 2). 4*H*-1,3,5-Selenadiazine ring system **E** was excluded out for the structure of **27a** by the ^{1}H NMR and ^{13}C NMR spectra because **27a** possessed non-equivalent two phenyl groups in the molecule. At first, **27a** was supposed to possess the 4*H*-1,2,5-selenadiazine ring system (**D**). It was rationalized that such products would be formed through the cycloaddition of 1,3-selenaza-1,3-butadienes **8** with *in situ* generated nitrile.[14] However, when a benzene solution of **6a** was heated in the presence of *p*-tolunitrile, the product compositions of the resulting reaction mixtures were essentially similar to those of the heating of **6a** in the absence of such additives, and no products, **27**–**30**, bearing *p*-tolyl substituents were found in the reaction mixture (Table 6). Thus, the plausible structure of **D** for **27** was also excluded. The structure of **27a** was finally determined by an X-ray crystallographic analysis, by which **27a** were shown to possess an unexpected 1,3,5-selenadiazine ring **C**, as shown below.

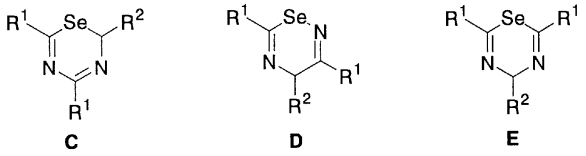


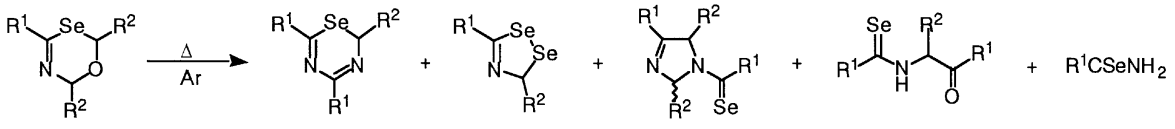
Chart 2. Possible Structures for **27**.

All results are given in Table 6.

X-ray Crystallographic Study of 27a. Pale-yellow crystals of **27a** were obtained on recrystallization from hexane-chloroform at room temperature; also, a single-crystal X-ray analysis demonstrated that **27a** possessed the 6*H*-1,3,5-selenadiazine ring bearing two phenyl groups at the C-2 and C-4 positions. In the crystal, there are mixed two isomers with two positions (equatorial and axial) in the methyl group at the C-6 position. The occupancy ratio is about 65:35 for two isomers with equatorial:axial positions. An ORTEP drawing of **27a** bearing an equatorial methyl group at the C-6 position is shown in Fig. 1, and the selected bond lengths and bond angles of **27a** are given in Tables 7 and 8.

These data show that the molecule of **27a** possessed, as a whole, a planar conformation and that the core six-membered ring possessed a distorted boat form in which C(1), N(1), C(2), and N(2) were almost planar and the Se(1) and C(3) atoms deviated by 0.318 Å and –0.635 Å, respectively. Two phenyl rings, [C(5)–C(10)] and [C(11)–C(16)], were shown to rotate by 20.2° and 15.1° from the central ring plane. All bond lengths and angles for the chemical structure of **27a** exhibited values within the normal range of common compounds. There is no

Table 6. Thermal Reaction of 6*H*-1,3,5-Oxaselenazines **6**



Substrate			Additive	Solvent	Temp	Time	Yields/%[a]				
R^1	R^2	**6**	(mol amt.)		/°C	/h	**27**	**28**	**29** (major : minor)[b]	**30**	**2**
C_6H_5	CH_3	**6a**	—	Benzene	Reflux	5	23 (**27a**)	29 (**28a**)	37 (**29a**, 2 : 1)	11 (**30a**)	0
C_6H_5	CH_3	**6a**	phenylacetylene (10)	Benzene	Reflux	2.5	13 (**27a**)	37 (**28a**)	33 (**29a**, 2 : 1)	trace (**30a**)	0
C_6H_5	CH_3	**6a**	*p*-tolunitrile (10)	Benzene	Reflux	3	trace (**27a**)	8 (**28a**)	79 (**29a**, 2 : 1)	trace (**30a**)	0
C_6H_5	CH_3	**6a**	Se (1.1)	Benzene	Reflux	2.5	58 (**27a**)	18 (**28a**)	22 (**29a**, 2 : 1)	trace (**30a**)	0
C_6H_5	t-C_4H_9	**6b**	—	Benzene	Reflux	5	10 (**27b**)	43 (**28b**)	0 (**29b**)	42 (**30b**)	0
p-ClC_6H_4	CH_3	**6c**	—	Benzene	Reflux	5	28 (**27c**)	24 (**28c**)	30 (**29c**, 2 : 1)	18 (**30c**)	0
C_6H_5	CH_3	**6a**	BF_3·OEt_2 (1.0)	CH_2Cl_2	R.T.	2.5	trace (**27a**)	7 (**28a**)	0 (**29b**)	0 (**30b**)	26 (**2a**)[c]

a) Isolated yields. b) Estimated by integration of the ^{1}H NMR spectrum. c) **6a** was recovered in 46% yield.

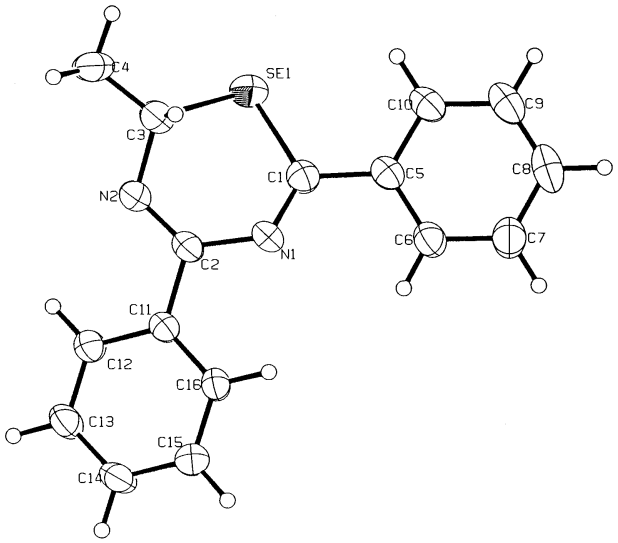


Figure 1. An ORTEP Drawing of **27a**.

short contact in the crystal structure.

Plausible Reaction Pathway of Thermal Reaction of 6*H*-1,3,5-Oxathiazines (5) and 6*H*-1,3,5-Oxaselenazines (6). 6*H*-1,3,5-Oxathiazines **5** and 6*H*-1,3,5-oxaselenazines **6** are known to cause retro-[4+2]-type thermal cycloreversion to generate 1,3-thiaza-1,3-butadienes **7** or 1,3-selenaza-1,3-butadienes **8**, respectively, bearing some electron-deficient or electron-donating groups at the C-4 positions of the heterodienes as stabilizing substituents. Our attempts were concentrated on the generation, isolation, or detection of such reactive species **7** lacking a factor of electronic stabilization; we obtained compounds **21**, **22**, and **23** by the thermal reaction of **5** bearing methyl groups at the C-4 and C-6 positions. Compounds **21** were an epimeric mixture of the [4+2]-type dimers of **7**, and compounds **22** were the epimeric mixture of the another [4+2]-type dimers of **7**, i.e. the cycloadducts of heterodienes **7** with the *in situ* generated double-bond isomers **25**. These results clearly showed that the double-bond isomerization of 1,3-thiaza-1,3-butadienes **7** bearing a methyl group at the C-4 positions might compete with the Diels–Alder dimerization of **7** under the thermal-reaction condition mentioned above. However, an alternative ionic stepwise dimerization mechanism initiated by the Michael-type nucleophilic attack of the sulfur atom of heterodiene **7** to afford **21** was not excluded at this time. A similar heating of **5** in the presence of thioacetamide or thiobenzamide (**1**) afforded **23** and **24** and, especially in such a case, **23** were obtained in much higher yields than the usual cases of thermal reactions of **5** in the absence of thioamides. These results indicated that **23** were assumed to have originated by the 1,4-addition of thioamides **1** to heterodienes **7**; also the formation of **24** is explained by a mechanism that includes a nucleophilic attack of the sulfur atom of thioamides at the C-4 position of heterodienes **7** and a subsequent ring closure accompanying the extrusion of H_2S. On the other hand, in all cases of thermal reactions starting from **5** bearing bulky and non-isomerizable *t*-butyl groups at the C-4 and C-6 positions, we only obtained complicated mixtures including a trace amount of **23** and **26**, and the ^{1}H NMR monitoring experiments of the thermal reaction of **5** in an NMR tube only gave unsuccessful results for the detection of heterodiene **7b** in the reaction mixture at all. However, when a solution of **5b** was heated in the presence of thioacetamide or thiobenzamide, **26b** was afforded in much higher yield. This result also suggested the nucleophilic addition of thioamides to the C-4 position of heterodiene **7b** followed by the thermal extrusion of nitriles from **F** to afford thiol-type in-

Table 7. Selected Bond Lengths (Å) for **27a**.[a)]

Atom–Atom	Distance	Atom–Atom	Distance	Atom–Atom	Distance	Atom–Atom	Distance
Se(1)–C(1)	1.904(5)	C(1)–C(5)	1.472(7)	C(5)–C(10)	1.397(7)	C(11)–C(16)	1.383(6)
Se(1)–C(3)	1.987(7)	C(2)–C(11)	1.487(6)	C(6)–C(7)	1.373(8)	C(12)–C(13)	1.388(7)
N(1)–C(1)	1.288(6)	C(3)–C(4)	1.40(1)	C(7)–C(8)	1.384(8)	C(13)–C(14)	1.376(8)
N(1)–C(2)	1.402(6)	C(3)–C(4′)	1.29(2)	C(8)–C(9)	1.352(9)	C(14)–C(15)	1.363(8)
N(2)–C(2)	1.273(6)	C(4)–C(4′)	1.59(2)	C(9)–C(10)	1.374(8)	C(15)–C(16)	1.385(7)
N(2)–C(3)	1.452(8)	C(5)–C(6)	1.382(7)	C(11)–C(12)	1.377(7)		

a) Distances are in Angstroms. Estimated standard deviations in the least significant figure are given in parentheses.

Table 8. Selected Bond Angles (deg) for **27a**[a)]

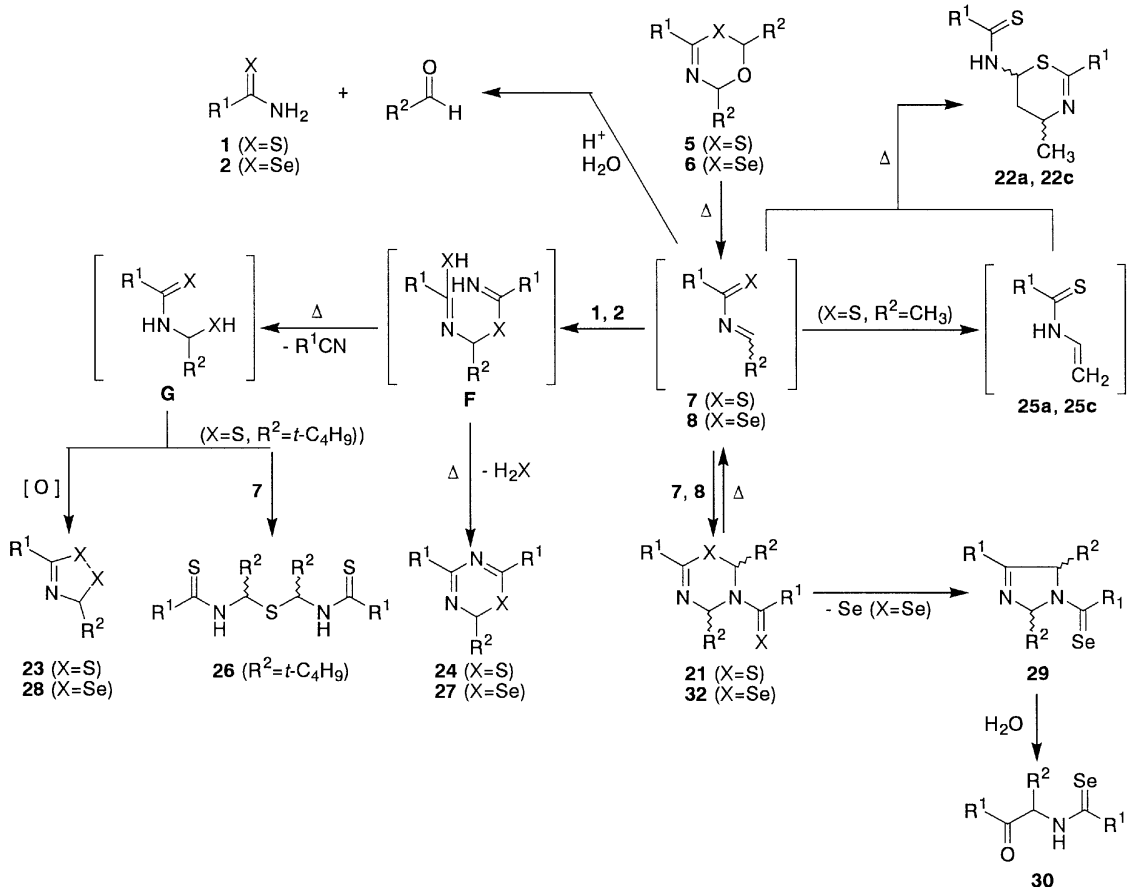
Atom–Atom–Atom	Angle	Atom–Atom–Atom	Angle	Atom–Atom–Atom	Angle
C(1)–Se(1)–C(3)	90.3(3)	Se(1)–C(3)–C(4′)	116(1)	C(7)–C(8)–C(9)	119.8(6)
C(1)–N(1)–C(2)	122.1(5)	N(2)–C(3)–C(4)	113.4(7)	C(8)–C(9)–C(10)	120.8(6)
C(2)–N(2)–C(3)	118.9(5)	N(2)–C(3)–C(4′)	123(1)	C(5)–C(10)–C(9)	120.5(6)
Se(1)–C(1)–N(1)	122.3(4)	C(4)–C(3)–C(4′)	73(1)	C(2)–C(11)–C(12)	120.5(5)
Se(1)–C(1)–N(5)	117.5(4)	C(3)–C(4)–C(4′)	50.6(8)	C(2)–C(11)–C(16)	120.6(5)
N(1)–C(1)–C(5)	120.2(5)	C(3)–C(4′)–C(4)	57(1)	C(12)–C(11)–C(16)	118.9(5)
N(1)–C(2)–N(2)	127.7(5)	C(1)–C(5)–C(6)	119.6(5)	C(11)–C(12)–C(13)	120.7(5)
N(1)–C(2)–C(11)	113.8(5)	C(1)–C(5)–C(10)	122.3(5)	C(12)–C(13)–C(14)	119.6(5)
N(2)–C(2)–C(11)	118.5(5)	C(6)–C(5)–C(10)	118.0(5)	C(13)–C(14)–C(15)	120.1(5)
Se(1)–C(3)–N(2)	110.1(5)	C(5)–C(6)–C(7)	120.8(6)	C(14)–C(15)–C(16)	120.3(5)
Se(1)–C(3)–C(4)	116.5(7)	C(6)–C(7)–C(8)	120.1(6)	C(11)–C(16)–C(15)	120.4(5)

a) Angles are in degrees. Estimated standard deviations in the least significant figure are given in parentheses.

termediates **G**. It was assumed that any further oxidative ring closure of **G** just gave **23**, and the further nucleophilic addition of **G** to another heterodiene **7b** also resulted in the formation of **26**. Thus, the formation of all products, **21**, **22**, **23**, **24**, and **26**, obtained by the thermal reactions of **5** was fully rationalized by the *in situ* generation of 1,3-thiaza-1,3-butadienes **7**.

The heating of 6*H*-1,3,5-oxaselenazines **6** in the absence of trapping agents afforded **27**, **28**, **29**, and **30** along with a small amount of selenoamides **2**. The heating of **6a** in the presence of an excess amount of *p*-tolunitrile, cyclohexene, phenylacetylene, maleic anhydride, or 2,3-dimethyl-1,3-butadiene also gave resulting reaction mixtures whose product composition was similar to that of the heating of **6a** in the absence of such additives; neither the [4+2]-cycloadducts of 1,3-selenaza-1,3-butadienes **8** with *p*-tolunitrile,[13] products **27**–**29** bearing *p*-tolyl substituents in place of a phenyl group, nor the [4+2]-cycloadducts of **8** with the alkene or alkyne were obtained. In addition, no cycloadducts of selenoaldehydes, generated through an alternative retro-[2+2+2]-type cycloreversion of **6**, with 2,3-dimethyl-1,3-butadiene were found at all in the crude products. A slight improvement in the yield of **28a** was achieved by heating **6a** in the presence of a selenating agent,[10] i.e. $(Me_3Si)_2Se$-$Et_2O{\cdot}BF_3$;[37] in this case small amounts of **27a**, **29a**, **30a**, and the unidentified compounds were also obtained along with **28a**. These results suggested that compounds **28** were afforded from **8** and selenating agents, i.e. selenoamides **2**,[10,11] which might be generated through a hydrolytic cleavage of **6** or **8** caused by a trace amount of water in the solvent or the atmosphere. The reaction of heterodienes **8** with selenoamides **2** might give the 1,4-addition products **F** in the primary stage, and **F** might undergo a thermal elimination of arylonitrile to give the intermediates **G**; also further oxidative ring closure of **G** in a similar route of the formation of **23** from **5** in the sulfur series finally gave **28**. The formation mechanism of **27** was also explained by the 1,4-addition of selenoamides **2** to heterodienes **8** as in an analogous course of formation of **24** from **7**. Interestingly, in contrast with the formation of **21** and **22** in the sulfur series, analogous [4+2]-type dimers of **8** were not found at all in the reaction mixture, and we just obtained unexpected products, **29** and **30**, besides **27** and **28**. The formation of [4+2]-type dimers **21** in the sulfur series strongly suggested that *in situ* generated heterodienes **8** also caused facile [4+2]-type dimerization to give **32** under the condition of the thermal reaction of **6**.[12] Thus, it was assumed that **29** were afforded through the thermal or oxidative selenium extrusion of dimers **32**. Selenoamides **30** were also suggested to be afforded by further hydrolytic ring cleavage of **29**. However, the ^{1}H NMR monitoring experiments of the thermal reaction of **6** in an NMR tube only gave discourageous results for the detection of **8** or **32** in the reaction mixture.

The plausible reaction paths for the formation of the products by thermal reactions of 6*H*-1,3,5-oxathiazines **5** and 6*H*-1,3,5-oxaselenazines **6** in the absence of trapping agents are summarized in Scheme 5. However, to date, all attempts to de-



Scheme 5.

tect or isolate heterodienes, **7** or **8**, or the intermediates, **F** or **G**, were not successful at all.

Conclusion. In conclusion, we found the generation of heterodienes, 1,3-thiaza-1,3-butadienes **7** and 1,3-selenaza-1,3-butadienes **8**, by retro-[4+2]-type thermal cycloreversion of 2,4,6-trisubstituted 6*H*-1,3,5-oxathiazines **5** or 6*H*-1,3,5-oxaselenazines **6**, respectively. Various applications of heterodienes **7** and **8** for the syntheses of chalcogen-containing heterocycles are in progress in our laboratory.

Experimental

Instruments. The melting points were determined with a Büchi 535 micro-melting-point apparatus. ^{1}H NMR spectra were recorded on a Bruker AC-400P (400 MHz) spectrometer, and the chemical shifts of the ^{1}H NMR spectra are given in δ relative to internal tetramethylsilane (TMS). ^{13}C NMR spectra were recorded on a Bruker AC-400P (100 MHz). ^{77}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 P_4O_{10} and were freshly distilled before use. Benzene, toluene, and hexane were dried over CaH_2 and were freshly distilled before use. Methanol, ethanol, and 2-propanol were dried over MgO and were freshly distilled before use. All substrates and reagents including benzonitrile, *p*-chlorobenzonitrile, *p*-tolunitrile, thiobenzamide (**1a**), thioacetamide, 2,4,6-trimethyl-1,3,5-trioxane (paraldehyde, **3**), pivalaldehyde (**4**), benzaldehyde, dimethyl acetylenedicarboxylate (DMAD), methyl propiolate, maleic anhydride, *p*-benzoquinone, diethyl azodicarboxylate (DEAD), tetracyanoethylene (TCNE), cyclohexene, phenylacetylene, 2,3-dimethyl-1,3-butadiene, benzenethiol, phenylmethanethiol, propylamine, boron trifluoride diethyl ether complex ($Et_2O{\cdot}BF_3$), *m*-chloroperbenzoic acid (*m*CPBA), elemental selenium, and sodium tetrahydroborate ($NaBH_4$) were commercially available reagent grade and were used without any pretreatment.

General Procedure for the Preparation of Arenecarboselenoamides (2). A dichloromethane solution of arylonitrile was treated with $(Me_3Si)_2Se$ (1.1 mol amt.) and $Et_2O{\cdot}BF_3$ (2.2 mol amt.)[43] under an Ar atmosphere, and the reaction mixture was heated to 60 °C for 8 h in a sealed tube. The reaction mixture was then quenched with an aqueous $NaHCO_3$ solution, and extracted with dichloromethane. The organic layer was washed with water, and then dried over anhydrous Na_2SO_4 powder. After removing the solvent in vacuo, the crude product was purified using column chromatography on silica gel to afford the corresponding arenecarboselenoamides (**2a**, **2c**) in 70–80% yields.

2a ($R^1 = C_6H_5$): Yellow needles, mp 124.0–124.5 °C (Ref. 51, 126.0–126.5 °C).

2c ($R^1 = p$-ClC_6H_4): Yellow needles, mp 126.0–128.0 °C (Ref. 51, 127.5–128.5 °C).

General Procedure for the Preparation of 2,6-Dialkyl-4-aryl-6*H*-1,3,5-oxathiazines (5) and 6*H*-1,3,5-Oxaselenazines (6). A 20 ml dichloromethane solution of arenecarbothioamide **1** (10.0 mmol) or arenecarboselenoamide **2** (10.0 mmol) was treated with 2,4,6-trimethyl-1,3,5-trioxane (paraldehyde, **3**, 1.04 g, 8.00 mmol) or pivalaldehyde (**4**, 2.06 g, 24.0 mmol) and $Et_2O{\cdot}BF_3$ (2.84 g, 20.0 mmol) at 0 °C, and the reaction mixture was stirred for 3 h at room temperature. The reaction was then quenched with an aqueous $NaHCO_3$ solution, and extracted with dichloromethane. The organic layer was washed with water, and then dried over anhydrous Na_2SO_4 powder. After removing the solvent in vacuo, the crude product was purified using column chromatography on silica gel to afford 2,6-dialkyl-4-aryl-6*H*-1,3,5-oxathiazine (**5**) or 2,6-dialkyl-4-aryl-6*H*-1,3,5-oxaselenazine (**6**), respectively, in good yields. Purification of solidified products **6b** and **6d** was achieved by recrystallization using hexane-dichloromethane.

5a ($R^1 = C_6H_5$, $R^2 = CH_3$): Pale yellow oil; MS *m*/*z* (%) 207 (M^+; 17), 165 (21), 39 (bp); IR (neat) 2985, 1614, 1447, 1373, 1323, 1231, 1161, 1114, 961, 766, 692 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.60 (3H, d, J = 6.1 Hz), 1.61 (3H, d, J = 6.2 Hz), 5.28 (1H, q, J = 6.2 Hz), 5.35 (1H, q, J = 6.1 Hz), 7.35–7.43 (3H, m), 7.78–7.80 (2H, m); ^{13}C NMR ($CDCl_3$) δ 22.2 (q), 22.5 (q), 75.6 (s), 87.4 (d), 126.2 (d), 128.3 (d), 130.7 (d), 138.5 (s), 157.0 (s). Found: C, 63.05; H, 6.54; N, 6.37%. Calcd for $C_{11}H_{13}NOS$: C, 63.74; H, 6.32; N, 6.76%.

5b ($R^1 = C_6H_5$, $R^2 = t$-C_4H_9): Colorless plates, mp 95.4–96.0 °C; MS *m*/*z* (%) 291 (M^+; 22), 41 (bp); IR (KBr) 2954, 2866, 1611, 1479, 1361, 1229, 1063, 767, 691 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.05 (9H, s), 1.06 (9H, s), 4.84 (1H, s), 4.98 (1H, s), 7.38–7.43 (3H, m), 7.84–7.87 (2H, m); ^{13}C NMR ($CDCl_3$) δ 25.1 (q), 25.3 (q), 36.0 (s), 36.8 (s), 88.6 (d), 96.8 (d), 126.3 (d), 128.1 (d), 130.6 (d), 139.2 (s), 157.5 (s). Found: C, 69.83; H, 8.66; N, 4.97%. Calcd for $C_{17}H_{25}NOS$: C, 70.06; H, 8.65; N, 4.81%.

5c ($R^1 = p$-ClC_6H_4, $R^2 = CH_3$): Colorless needles, mp 101.9–102.5 °C (dec.); MS *m*/*z* (%) 197 ($M^+ - CH_3CHO$; 17), 58 (bp); IR (KBr) 2979, 1606, 1489, 1398, 1311, 1238, 1230, 1162, 1089, 965, 846, 838, 827 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.61 (3H, d, J = 6.3 Hz), 1.64 (3H, d, J = 6.3 Hz), 5.30 (1H, q, J = 6.3 Hz), 5.36 (1H, q, J = 6.3 Hz), 7.37 (2H, d, J = 8.9 Hz), 7.74 (2H, d, J = 8.9 Hz); ^{13}C NMR ($CDCl_3$) δ 22.2 (q), 22.5 (q), 75.8 (d), 87.5 (d), 127.6 (s), 128.6 (d), 136.9 (s), 137.0 (s), 156.0 (s). Found: C, 54.73; H, 4.97; N, 5.75%. Calcd for $C_{11}H_{12}ClNOS$: C, 54.66; H, 5.00; N, 5.79%.

5d ($R^1 = p$-ClC_6H_4, $R^2 = t$-C_4H_9): Colorless crystals, mp 95.4–96.0 °C (dec.); MS *m*/*z* (%) 325 (M^+; 2), 268 ($M^+ - t$-C_4H_9; 2), 239 ($M^+ - t$-C_4H_9CHO; 17), 41 (bp); IR (KBr) 2954, 2866, 1611, 1479, 1229, 1063, 767, 691 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.05 (9H, s), 1.06 (9H, s), 4.81 (1H, s), 4.96 (1H, s), 7.35 (2H, d, J = 8.6 Hz), 7.79 (2H, d, J = 8.6 Hz); ^{13}C NMR ($CDCl_3$) δ 25.1 (q), 25.3 (q), 36.0 (s), 36.8 (s), 88.7 (d), 96.8 (d), 127.5 (d), 128.3 (d), 136.6 (s), 137.5 (s), 156.3 (s). Found: C, 62.39; H, 7.29; N, 4.49%. Calcd for $C_{17}H_{24}ClNOS$: C, 62.65; H, 7.42; N, 4.30%.

6a ($R^1 = C_6H_5$, $R^2 = CH_3$):[44] Orange oil; MS *m*/*z* (%) 257 (M^+; 50, ^{80}Se), 213 (bp); IR (neat) 3059, 2982, 2923, 1602, 1533, 1447, 1314, 1223, 1116, 951, 764, 691 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.63 (3H, d, J = 6.2 Hz), 1.72 (3H, d, J = 6.2 Hz), 5.11 (1H, q, J = 6.2 Hz), 5.57 (1H, q, J = 6.2 Hz), 7.23–7.38 (3H, m), 7.72–7.74 (2H, m); ^{13}C NMR ($CDCl_3$) δ 22.9 (q), 23.7 (q), 73.1 (d), 89.3 (s), 126.2 (d), 128.2 (d), 130.6 (d), 140.0 (s), 157.5 (s). Found: C, 51.45; H, 5.01; N, 5.40%. Calcd for $C_{11}H_{13}NOSe$: C, 51.98; H, 5.15; N, 5.51%.

6b ($R^1 = C_6H_5$, $R^2 = t$-C_4H_9):[44] Pale yellow needles, mp 94.0–95.0 °C (Ref. 44, 98.0–98.5 °C); MS *m*/*z* (%) 252 ($M^+ - t$-BuCHO – 1; 14, ^{80}Se), 42 (bp); IR (neat) 2953, 1622, 1479, 1392, 1165, 1073, 1058, 999, 764, 694 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.06 (9H, s), 1.08 (9H, s), 4.61 (1H, s), 5.41 (1H, s), 7.35–7.41 (3H, m), 7.79–7.82 (2H, m); ^{13}C NMR ($CDCl_3$) δ 25.3 (q), 25.5 (q), 36.4 (s), 36.9 (s), 89.0 (s), 99.0 (br. s), 126.6 (d), 128.3 (d), 130.6 (d), 140.7

(s), 157.9 (s). Found: C, 59.84; H, 7.27; N, 4.02%. Calcd for $C_{17}H_{25}NOSe$: C, 60.35; H, 7.45; N, 4.14%.

6c ($R^1 = p$-ClC_6H_4, $R^2 = CH_3$): Pale yellow needles, mp 88.7–89.1 °C; MS *m/z* (%) 245 (M^+ – MeCHO; 79, ^{80}Se), 108 (bp); IR (KBr) 2976, 2921, 1607, 1487, 1397, 1225, 1163, 1089, 1058, 955, 828, 582 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.64 (3H, d, J = 6.2 Hz), 1.78 (3H, d, J = 6.0 Hz), 5.15 (1H, q, J = 6.2 Hz), 5.65 (1H, q, J = 6.0 Hz), 7.34–7.37 (2H, m), 7.66–7.69 (2H, m); ^{13}C NMR ($CDCl_3$) δ 22.9 (q), 23.8 (q), 73.5 (d), 89.5 (s), 127.7 (d), 128.6 (d), 136.8 (s), 138.5 (s), 156.5 (s). Found: C, 45.78; H, 4.18; N, 4.87%. Calcd for $C_{11}H_{12}ClNOSe$: C, 45.77; H, 4.19; N, 4.85%.

Thermal Reaction of 6*H*-1,3,5-Oxathiazines (5) or 6*H*-1,3,5-Oxaselenazines (6) in the Presence of an Acetylenic Dienophile, *p*-Benzoquinone, or Diethyl Azodicarboxylate (DEAD). After a 50 ml benzene solution of 6*H*-1,3,5-oxathiazine (**5**, 2.00 mmol) or 6*H*-1,3,5-oxaselenazine (**6**, 2.00 mmol) was treated with a trappimg agent (10.0 mmol), such as dimethyl acetylenedicarboxylate (DMAD), methyl propiolate, *p*-benzoquinone, or diethyl azodicarboxylate (DEAD), the reaction mixture was heated at refluxing temperature for several hours. The reaction mixture was then cooled to room temperature, quenched with an aqueous NaOH solution, and extracted with benzene. The organic layer was washed with water, and then dried over anhydrous Na_2SO_4 powder. After removing the solvent in vacuo, the crude product was purified by using column chromatography on silica gel to afford the cycloadducts in high-to-moderate yields.

9a ($R^1 = C_6H_5$, $R^2 = CH_3$, $R^3 = R^4 = CO_2CH_3$): Pale yellow oil; MS *m/z* (%) 305 (M^+; 3), 202 (bp); IR (neat) 2953, 1732, 1635, 1435, 1267, 940, 767, 692 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.48 (3H, d, J = 6.9 Hz), 3.84 (3H, s), 3.85 (3H, s), 4.92 (1H, q, J = 6.9 Hz), 7.28–7.49 (3H, m), 7.88–7.91 (2H, m); ^{13}C NMR ($CDCl_3$) δ 16.0 (q), 52.6 (q), 53.1 (q), 57.3 (s), 127.4 (d), 128.5 (d), 129.0 (s), 131.4 (d), 135.9 (s), 156.1 (s), 163.2 (s), 165.7 (s). Found: C, 58.94; H, 4.86; N, 4.70%. Calcd for $C_{15}H_{15}NO_4S$: C, 59.00; H, 4.95; N, 4.59%.

9b ($R^1 = C_6H_5$, $R^2 = t$-C_4H_9, $R^3 = R^4 = CO_2CH_3$): Colorless needles, mp 86.2–86.3 °C (dec.); MS *m/z* (%) 348 (M^+ + 1; 2), 292 ($M^+ + 1 - C_4H_8$; 55), 75 (bp); IR (neat) 3089, 2976, 1724, 1643, 1435, 1264, 1046, 992, 936, 767 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.05 (9H, s), 3.80 (3H, s), 3.86 (3H, s), 5.27 (1H, s), 7.35–7.55 (3H, m), 7.85–7.90 (2H, m); ^{13}C NMR ($CDCl_3$) δ 26.5 (q), 42.3 (s), 52.6 (q), 53.1 (q), 70.8 (d), 126.2 (s), 127.3 (d), 128.6 (d), 131.4 (d), 131.9 (s), 136.4 (s), 153.1 (s), 164.3 (s), 167.4 (s). Found: C, 62.28; H, 6.11; N, 3.98%. Calcd for $C_{18}H_{21}NO_4S$: C, 62.23; H, 6.09; N, 4.03%.

10a ($R^1 = C_6H_5$, $R^2 = CH_3$, $R^3 = CO_2CH_3$, $R^4 = H$): Pale yellow plates, mp 68.0–69.0 °C; MS *m/z* (%) 247 (M^+; 8), 144 (bp); IR (KBr) 2980, 1698, 1439, 1289, 1236, 1219, 1059, 936, 769, 752, 691 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.31 (3H, d, J = 6.9 Hz), 3.80 (3H, s), 5.44 (qd, J = 6.9, 1.4 Hz), 7.39–7.48 (3H, m), 7.69 (1H, d, J = 1.4 Hz), 7.83–7.86 (2H, m); ^{13}C NMR ($CDCl_3$) δ 16.9 (q), 52.0 (q), 52.9 (s), 123.9 (s), 127.1 (d), 128.5 (d), 131.0 (d), 131.1 (d), 136.8 (s), 153.0 (s), 163.9 (s). Found: C, 63.07; H, 5.21; N, 5.67%. Calcd for $C_{13}H_{13}NO_2S$: C, 63.13; H, 5.21; N, 5.62%.

11a ($R^1 = C_6H_5$, $R^2 = CH_3$, $R^3 = R^4 = CO_2CH_3$): Yellow oil; MS *m/z* (%) 354 (M^+ + 1; 13, ^{80}Se), 250 (bp), 218 (97); IR (neat) 2952, 1729, 1617, 1434, 1255, 765, 692 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.59 (3H, d, J = 7.0 Hz), 3.84 (3H, s), 3.86 (3H, s), 4.52 (1H, q, J = 7.0 Hz), 7.38–7.49 (3H, m), 7.82–7.85 (2H, m); ^{13}C NMR ($CDCl_3$) δ 15.8 (q), 52.6 (q), 53.1 (q), 62.3 (d), 127.9 (d), 128.3 (s), 128.7 (d), 131.4 (d), 136.4 (s), 137.3 (s), 158.5 (s), 164.0 (s), 166.2 (s). Found: C, 51.42; H, 4.31; N, 4.28%. Calcd for $C_{15}H_{15}NO_4Se$: C, 51.15; H, 4.29; N, 3.98%.

11b ($R^1 = C_6H_5$, $R^2 = t$-C_4H_9, $R^3 = R^4 = CO_2CH_3$): Yellow oil; MS *m/z* (%) 316 (M^+ – Se + 1; bp); IR (neat) 3324, 2953, 1716, 1488, 1440, 1237, 1208, 1133, 1072, 763, 698 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.39 (9H, s), 3.67 (3H, s), 3.83 (3H, s), 7.34–7.37 (3H, m), 7.47–7.49 (2H, m), 8.54 (1H, s); ^{13}C NMR ($CDCl_3$) δ 29.5 (q), 32.5 (s), 51.3 (q), 51.9 (q), 112.3 (s), 113.3 (s), 128.16 (d), 128.22 (d), 128.5 (d), 131.2 (s), 133.0 (s), 140.8 (s), 165.1 (s), 167.6 (s). The signal, revealed at δ 8.54, disappeared upon a similar ^1H NMR measurement of **11b** using $CDCl_3$ and a small amount of CD_3OD. All of the spectral data strongly suggested a highly conjugated enolic structure for **11b**. Found: C 54.39; H, 5.13; N, 3.40%. Calcd for $C_{18}H_{21}NO_4Se$: C, 54.83; H, 5.37; N, 3.55%.

11c ($R^1 = p$-ClC_6H_4, $R^2 = CH_3$, $R^3 = R^4 = CO_2CH_3$): Orange oil; MS *m/z* (%) 387 (M^+; 5, ^{80}Se), 328 (11), 250 (84), 218 (bp); IR (neat) 2951, 1716, 1591, 1251, 834, 582 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.59 (3H, d, J = 7.0 Hz), 3.84 (3H, s), 3.86 (3H, s), 4.47 (1H, q, J = 7.0 Hz), 7.37–7.40 (2H, m), 7.77–7.79 (2H, m); ^{13}C NMR ($CDCl_3$) δ 15.8 (q), 52.7 (q), 53.0 (q), 62.5 (d), 127.9 (s), 128.8 (d), 129.1 (d), 135.7 (s), 136.9 (s), 137.6 (s), 157.5 (s), 163.7 (s), 166.1 (s). Found: C, 46.90; H, 3.60; N, 3.75%. Calcd for $C_{15}H_{14}ClNO_4Se$: C, 46.59; H, 3.65; N, 3.62%.

12a ($R^1 = C_6H_5$, $R^2 = CH_3$, $R^3 = CO_2CH_3$, $R^4 = H$): Yellow oil; MS *m/z* (%) 296 (M^+ + 1; 10, ^{80}Se), 192 (bp), 160 (32), 131 (37); IR (KBr) 2950, 1713, 1435, 1280, 1050, 910, 745, 651, 621 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.30 (3H, d, J = 7.0 Hz), 3.80 (3H, s), 5.65 (1H, q, J = 7.0 Hz), 7.39–7.48 (3H, m), 7.77–7.79 (2H, m), 8.24 (1H, s); ^{13}C NMR ($CDCl_3$) δ 15.3 (q), 52.1 (q), 56.0 (d), 125.8 (s), 127.4 (d), 128.6 (d), 131.0 (d), 131.4 (d), 138.3 (s), 152.8 (s), 163.4 (s). Found: C, 53.31; H, 4.48; N, 4.68%. Calcd for $C_{13}H_{13}NO_2Se$: C, 53.07; H, 4.45; N, 4.76%.

12c ($R^1 = p$-ClC_6H_4, $R^2 = CH_3$, $R^3 = CO_2CH_3$, $R^4 = H$): Orange oil; MS *m/z* (%) 329 (M^+; 8, ^{80}Se), 248 (5), 192 (bp), 160 (45), 132 (51); IR (neat) 2950, 1713, 1435, 1280, 1051, 917, 832, 746, 711, 591, 555 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.28 (3H, d, J = 6.9 Hz), 3.80 (3H, s), 5.64 (1H, q, J = 6.9 Hz), 7.36–7.38 (2H, m), 7.71–7.73 (2H, m), 8.21 (1H, s); ^{13}C NMR ($CDCl_3$) δ 15.2 (q), 52.1 (q), 56.1 (d), 125.8 (s), 128.6 (d), 128.7 (d), 130.9 (d), 136.6 (s), 137.1 (s), 151.6 (s), 163.2 (s). Found: C, 47.58; H, 3.63; N, 4.35%. Calcd for $C_{13}H_{12}ClNO_2Se$: C, 47.51; H, 3.68; N, 4.26%.

13a ($R^1 = C_6H_5$, $R^2 = CH_3$): Red needles, mp 126.0–127.0 °C; MS *m/z* (%) 317 (M^+; 53, ^{80}Se), 212 (bp); IR (KBr) 3056, 1650, 1587, 1292, 889, 841, 770, 693 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.30 (3H, d, J = 7.0 Hz), 5.87 (1H, q, J = 7.0 Hz), 6.80 (1H, d, J = 10.0 Hz), 6.89 (1H, d, J = 10.0 Hz), 7.40–7.50 (3H, m), 7.80–7.83 (2H, m); ^{13}C NMR ($CDCl_3$) δ 15.3 (q), 55.7 (d), 127.4 (d), 128.7 (d), 131.4 (d), 135.9 (dd), 136.7 (s), 137.0 (dd), 138.0 (s), 141.7 (s), 154.6 (s), 181.0 (s), 182.7 (s). Found: C, 57.03; H, 3.50; N, 4.27%. Calcd for $C_{15}H_{11}NO_2Se$: C, 56.97; H, 3.51; N, 4.43%.

14a ($R^1 = C_6H_5$, $R^2 = CH_3$): Pale yellow oil; MS *m/z* (%) 385 (M^+; 0.4, ^{80}Se), 43 (bp); IR (neat) 2984, 2936, 1733, 1713, 1627, 1447, 1374, 1283, 1091, 1039, 908, 764, 692, 592 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.27–1.34 (6H, m), 1.56 (3H, d, J = 6.3 Hz), 4.23–4.31 (4H, m), 6.40 (1H, q, J = 6.3 Hz), 7.39–7.49 (3H, m), 7.57–7.59 (2H, m); ^{13}C NMR ($CDCl_3$) δ 14.3 (q), 14.5 (q), 18.6 (q), 41.5 (d), 63.3 (t), 63.8 (t), 125.6 (d), 129.0 (d), 131.6 (d), 137.5 (s), 150.5 (s), 154.8 (s), 155.3 (s). Found: C, 47.03; H, 5.02; N, 10.50%. Calcd for $C_{15}H_{19}N_3O_4Se$: C, 46.88; H, 4.98; N, 10.93%.

Heating of 6*H*-1,3,5-Oxathiazine (5) or 6*H*-1,3,5-Ozaselenazines (6) in an Alcoholic Media. An alcoholic solution (20 ml) of 6*H*-1,3,5-oxathiazine (**5**, 2.00 mmol) or 6*H*-1,3,5-oxaselenazine (**6**, 2.00 mmol) was heated at refluxing temperature for a several

hours. After cooling to room temperature and quenching with water, the reaction mixture was subjected to the usual workup. The crude product was purified using column chromatography on silica gel to afford *N*-(1-alkoxyethyl)arenecarbothioamide (**15**, **16**) or *N*-(1-alkoxyalkyl)arenecarboselenoamides (**17**, **18**) as major products.

15b ($R^1 = C_6H_5$, $R^2 = t\text{-}C_4H_9$, Nu = OC_2H_5): Yellow oil; MS *m/z* (%) 251 (M^+; 50), 222 ($M^+ - C_2H_5$; 84), 207 ($M^+ - OC_2H_5$; 91), 87 (bp); IR (neat) 3397, 3290, 2963, 2904, 1501, 1481, 1449, 1370, 1362, 1116, 1069, 961, 736, 693 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.04 (9H, s), 1.21 (3H, br. t, J = 6.9 Hz), 3.64 (1H, dq, J = 9.9, 7.0 Hz), 3.73 (1H, dq, J = 9.9, 6.9 Hz), 5.81 (1H, d, J = 8.0 Hz), 7.30–7.50 (3H, m), 7.55–7.70 (1H, m), 7.72–7.75 (2H, m); ^{13}C NMR ($CDCl_3$) δ 15.0 (q), 24.9 (q), 36.5 (s), 64.7 (t), 90.4 (d), 126.4 (d), 128.5 (d), 131.1 (d), 142.3 (s), 200.9 (s). Found: C, 66.85; H, 8.76; N, 5.40%. Calcd for $C_{14}H_{21}NOS$: C, 66.89; H, 8.42; N, 5.57%.

16a ($R^1 = C_6H_5$, $R^2 = CH_3$, Nu = O*i*-C_3H_7): Yellow powder, mp 66.2–66.3 °C; MS *m/z* (%) 223 (M^+; 5), 121 (bp); IR (KBr) 3253, 2976, 1710, 1519, 1447, 1379, 1245, 1109, 1086, 999, 965, 725, 697 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.21 (3H, d, J = 6.2 Hz), 1.25 (3H, d, J = 6.2 Hz), 1.50 (3H, d, J = 5.8 Hz), 3.96 (1H, septet, J = 6.2 Hz), 6.13 (dq, J = 8.2, 5.8 Hz), 7.38–7.49 (3H, m), 7.64 (1H, br. s), 7.73–7.75 (2H, m); ^{13}C NMR ($CDCl_3$) δ 21.3 (q), 21.9 (q), 23.3 (q), 70.4 (d), 81.1 (d), 126.5 (d), 128.5 (d), 131.3 (d), 141.5 (s), 198.5 (s). Found: C, 64.49; H, 7.93; N, 6.22%. Calcd for $C_{12}H_{17}NOS$: C, 64.53; H, 7.67; N, 6.27%.

17a ($R^1 = C_6H_5$, $R^2 = CH_3$, Nu = OCH_3): Yellow oil; MS *m/z* (%) 243 (M^+; bp, ^{80}Se), 211 ($M^+ - CH_3OH$; 64, ^{80}Se), 185 (83), 104 (95); IR (neat) 3211, 2989, 1510, 1449, 1378, 1131, 1093, 693 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.55 (3H, d, J = 5.8 Hz), 3.53 (3H, s), 6.06 (1H, dq, J = 8.4, 5.8 Hz), 7.36–7.53 (3H, m), 7.75–7.77 (2H, m), 8.05 (1H, br.s); ^{13}C NMR ($CDCl_3$) δ 20.3 (q), 57.1 (q), 87.9 (d), 126.4 (d), 128.6 (d), 131.4 (d), 144.8 (s), 204.7 (s). Found: C, 49.16; H, 5.29; N, 5.66%. Calcd for $C_{10}H_{13}NOSe$: C, 49.60; H, 5.41; N, 5.78%.

18a ($R^1 = C_6H_5$, $R^2 = CH_3$, Nu = OC_2H_5): Yellow needles, mp 94.0–95.0 °C; MS *m/z* (%) 257 (M^+; 11, ^{80}Se), 211 ($M^+ - C_2H_5OH$; 15, ^{80}Se), 44 (bp); IR (KBr) 3241, 2980, 1510, 1483, 1448, 1231, 1113, 1087, 1054, 693, 675 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.25 (3H, d, J = 7.0 Hz), 1.55 (3H, d, J = 5.8 Hz), 3.68–3.84 (2H, m), 6.13 (1H, dq, J = 8.1, 5.8 Hz), 7.35–7.51 (3H, m), 7.73–7.75 (2H, m), 8.14 (1H, br. s); ^{13}C NMR ($CDCl_3$) δ 15.2 (q), 20.5 (q), 65.0 (t), 86.3 (d), 126.4 (d), 128.5 (d), 131.3 (d), 144.7 (s), 203.9 (s). Found: C, 51.48; H, 6.04; N, 5.44%. Calcd for $C_{11}H_{15}NOSe$: C, 51.57; H, 5.90; N, 5.47%.

18b ($R^1 = C_6H_5$, $R^2 = t\text{-}C_4H_9$, Nu = OC_2H_5): Orange oil; MS *m/z* (%) 297 (M^+; 12, ^{80}Se), 115 (bp); IR (neat) 3376, 3250, 2963, 1503, 1481, 1447, 1372, 1112, 1063, 695 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.07 (9H, s), 1.23 (3H, t, J = 7.0 Hz), 3.70 (1H, dq, J = 10.0, 7.0 Hz), 3.77 (1H, dq, J = 10.0, 7.0 Hz), 5.95 (1H, d, J = 9.4 Hz), 7.36–7.52 (3H, m), 7.73–7.75 (2H, m), 8.05 (1H, br. s); ^{13}C NMR ($CDCl_3$) δ 15.1 (q), 25.0 (q), 36.6 (s), 65.1 (t), 93.5 (d), 126.3 (d), 128.7 (d), 131.2 (d), 145.7 (s), 206.5 (s). Found: C, 56.14; H, 7.30; N, 4.41%. Calcd for $C_{14}H_{21}NOSe$: C, 56.37; H, 7.10; N, 4.70%.

17c ($R^1 = p\text{-}ClC_6H_4$, $R^2 = CH_3$, Nu = OCH_3): Yellow needles, mp 101.0–102.0 °C; MS *m/z* (%) 277 (M^+; 15, ^{80}Se), 246 ($M^+ - OCH_3$; 10, ^{80}Se), 59 (bp); IR (KBr) 3254, 2988, 2930, 1588, 1510, 1481, 1399, 1372, 1238, 1132, 1086, 1039, 883, 822, 719 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.53 (3H, d, J = 5.8 Hz), 3.50 (3H, s), 5.59 (1H, dq, J = 8.1, 5.8 Hz), 7.30–7.33 (2H, m), 7.66–7.69 (2H, m), 8.22 (1H, br. s); ^{13}C NMR ($CDCl_3$) δ 20.1 (q), 57.0 (q), 87.9 (d), 127.7 (d), 128.5 (d), 137.4 (s), 142.8 (s), 202.8 (s). Found: C, 43.48; H, 4.49; N, 4.93%. Calcd for $C_{10}H_{12}ClNOSe$: C, 43.42; H, 4.37; N, 5.06%.

18c ($R^1 = p\text{-}ClC_6H_4$, $R^2 = CH_3$, Nu = OC_2H_5): Yellow needles, mp 85.0–86.0 °C; MS *m/z* (%) 289 (M^+; 4, ^{80}Se), 246 (8), 44 (bp); IR (KBr) 3222, 2977, 1589, 1515, 1481, 1404, 1374, 1231, 1110, 1093, 1052, 932, 725 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.24 (3H, t, J = 7.0 Hz), 1.53 (3H, d, J = 5.8 Hz), 3.65–3.81 (2H, m), 6.08 (1H, dq, J = 7.9, 5.8 Hz), 7.29–7.31 (2H, m), 7.65–7.67 (2H, m), 8.27 (1H, br. s); ^{13}C NMR ($CDCl_3$) δ 15.1 (q), 20.3 (q), 64.9 (t), 86.4 (d), 127.6 (d), 128.5 (d), 137.3 (s), 142.7 (s), 202.1 (s). Found: C, 45.43; H, 4.88; N, 4.78%. Calcd for $C_{11}H_{14}ClNOSe$: C, 45.46; H, 4.85; N, 4.82%.

Heating of 6*H*-1,3,5-Oxaselenazines (6) in the Presence of a Thiol. After a benzene solution (20 ml) of 6*H*-1,3,5-oxaselenazine (**6**, 2.00 mmol) was treated with an excess amount of benzenethiol or phenylmethanethiol (20 mmol), the reaction mixture was heated at refluxing temperature for 4 h. Then, after cooling to room temperature and quenching with an aqueous NaOH solution, the reaction mixture was subjected to the usual workup. The crude product was purified using column chromatography on silica gel to afford *N*-(1-arylthioethyl)selenobenzamide (**19a**) or *N*-(1-alkylthioethyl)selenobenzamide (**20a**), respectively, in good yields.

19a ($R^1 = C_6H_5$, $R^2 = CH_3$, Nu = SC_6H_5): Orange oil; MS *m/z* (%) 321 (M^+; 2, ^{80}Se), 211 ($M^+ - C_6H_5SH$; 38, ^{80}Se), 66 (bp); IR (neat) 3210, 2979, 1583, 1483, 1447, 1361, 1246, 1124, 1025, 878, 765, 691, 570 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.74 (3H, d, J = 6.7 Hz), 6.37 (1H, dq, J = 8.5, 6.7 Hz), 7.25–7.33 (5H, m), 7.42–7.46 (3H, m), 7.49–7.51 (2H, m), 8.12 (1H, br. s); ^{13}C NMR ($CDCl_3$) δ 19.9 (q), 60.8 (d), 126.3 (d), 127.8 (d), 128.5 (d), 129.3 (d), 131.2 (d), 131.5 (d), 132.0 (s), 144.7 (s), 203.5 (s). Found: C, 56.69; H, 4.74; N, 4.18%. Calcd for $C_{15}H_{15}NSSe$: C, 56.25; H, 4.72; N, 4.37%.

20a ($R^1 = C_6H_5$, $R^2 = CH_3$, Nu = $SCH_2C_6H_5$): Red oil; MS *m/z* (%) 342 (M^+; 37, ^{80}Se), 211 ($M^+ - C_6H_5CH_2SH$; 38, ^{80}Se), 66 (bp); IR (neat) 3333, 3210, 3059, 3027, 2980, 2923, 1507, 1483, 1448, 1362, 1237, 1120, 1034, 877, 767, 694, 661, 570 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.61 (3H, d, J = 6.8 Hz), 3.86 (1H, d, J = 14.0 Hz), 3.97 (1H, d, J = 14.0 Hz), 6.08 (1H, dq, J = 8.5, 6.8 Hz), 7.19–7.34 (7H, m), 7.44–7.49 (3H, m), 7.99 (1H, br. s); ^{13}C NMR ($CDCl_3$) δ 20.2 (q), 36.2 (t), 60.4 (d), 126.5 (d), 127.2 (d), 128.4 (d), 128.7 (d), 128.8 (d), 131.2 (d), 138.2 (s), 144.2 (s), 202.6 (s). Found: C, 57.09; H, 5.16; N, 4.10%. Calcd for $C_{16}H_{17}NSSe$: C, 57.48; H, 5.12; N, 4.19%.

Heating of 6*H*-1,3,5-Oxaselenazines (6a) in the Presence of Propylamine. After a benzene solution (30 ml) of 6*H*-1,3,5-oxaselenazine **6a** (508 mg, 2.00 mmol) was treated with an excess amount of propylamine (1.30 g, 22.0 mmol), the reaction mixture was heated at refluxing temperature for 4 h or was kept standing at room temperature with stirring for 4 h. Then, after cooling to room temperature and quenching with water, the reaction mixture was subjected to the usual workup. The crude product was purified by using column chromatography on silica gel to afford *N*-propylselenobenzamide (253 mg, 56%) as a major product.

Thermal Reaction of 6*H*-1,3,5-Oxathiazines (5a). A toluene solution (20 ml) of 6*H*-1,3,5-oxathiazine (**5a** or **5c**, 2.00 mmol) was heated at refluxing temperature for 3 h. After cooling to room temperature, the solvent was removed in vacuo. The crude product was then purified by using column chromatography on silica gel to afford 5,6-dihydro-4*H*-1,3,5-thiadiazines **21**, 5,6-dihydro-4*H*-1,3-thiazines **22**, 3*H*-1,2,4-dithiazoles **23**, and 6*H*-1,3,5-thiadiazines **24** besides several unidentified products.

21a ($R^1 = C_6H_5$, $R^2 = CH_3$): Yellow oil; MS *m/z* (%) 265 ($M^+ - C_2H_6S$; 3,), 205 ($M^+ - C_7H_5S$; 0.8), 163 ($M^+/2$; bp), 131 ($M^+/2 - S$;

5); IR (neat) 2984, 1620, 1444, 1402, 1271, 952, 759, 693 cm^{-1}; ^1H NMR ($CDCl_3$, –30 °C) major-**21a**:minor-**21a** = 4:1, major isomer δ 1.71 (3H, d, J = 6.9 Hz), 1.77 (3H, d, J = 6.9 Hz), 1.90 (3H, d, J = 6.9 Hz), 1.98 (3H, d, J = 6.9 Hz), 5.60 (1H, q, J = 6.9 Hz), 5.88 (1H, q, J = 6.9 Hz), 7.08 (1H, q, J = 6.9 Hz), 7.26–7.30 (2H, m), 7.44–7.58 (4H, m), 7.83–7.85 (2H, m); ^{13}C NMR ($CDCl_3$, –30 °C) δ 21.2 (q), 22.9 (q), 23.2 (q), 23.7 (q), 52.9 (d), 70.0 (d), 71.1 (d), 124.2 (d), 125.0 (d), 127.0 (d), 128.6 (d), 129.0 (d), 131.4 (d), 137.8 (s), 153.5 (d), 198.2 (s), 201.3 (s). Found: C, 66.22; H, 5.50; N, 8.31%. Calcd for $C_{18}H_{18}N_2S_2$: C, 66.22; H, 5.56; N, 8.58%.

21c (R^1 = *p*-ClC_6H_4, R^2 = CH_3): Yellow needles, mp 63.8–64.4 °C (dec.); MS *m/z* (%) 396 (M^+; 1), 229 ($M^+ - C_9H_5ClS$; 10) 196 ($M^+/2$; bp); IR (KBr) 2985, 1714, 1621, 1592, 1488, 1399, 1091, 834 cm^{-1}; ^1H NMR ($CDCl_3$, –30 °C) major-**21c**:minor-**21c** = 2:1, major isomer δ 1.71 (3H, d, J = 6.9 Hz), 1.77 (3H, d, J = 6.8 Hz), 1.88 (3H, d, J = 7.0 Hz), 1.95 (3H, d, J = 6.9 Hz), 5.57 (1H, q, J = 10.1 Hz), 5.82 (1H, q, J = 10.4 Hz), 7.03 (1H, q, J = 10.2 Hz), 7.21–7.29 (1H, m), 7.36–7.47 (5H, m), 7.79 (2H, d, J = 8.5 Hz); ^{13}C NMR ($CDCl_3$, –30 °C) δ 21.1 (q), 22.8 (q), 23.1 (q), 23.7 (q), 53.0 (d), 55.8 (d), 70.2 (d), 71.1 (d), 125.7 (d), 126.7 (d), 128.7 (d), 128.9 (d), 129.1 (d), 129.3 (d), 134.9 (s), 136.0 (s), 137.4 (s), 140.9 (s), 152.2 (s), 155.2 (s), 196.8 (s), 200.0 (s). Found: C, 55.06; H, 4.09; N, 7.04%. Calcd for $C_{18}H_{16}Cl_2N_2S_2$: C, 54.68; H, 4.08; N, 7.09%.

22a (R^1 = C_6H_5, R^2 = CH_3): Yellow crystals, mp 178.1–179.5 °C (dec.); MS *m/z* (%) 326 (M^+; 2), 294 ($M^+ - S$; 1), 189 ($M^+ - C_6H_5CSN$; bp); IR (KBr) 3265, 2968, 1705, 1606, 1448, 1362, 1229, 942, 768, 694 cm^{-1}; ^1H NMR ($CDCl_3$) major-**22a**:minor-**22a** = 4:3, major isomer δ 1.54 (3H, d, J = 6.9 Hz), 1.79 (1H, ddd, J = 14.4, 10.8, 4.0 Hz), 2.35 (1H, ddd, J = 14.2, 4.2, 3.2 Hz), 3.74 (1H, qdd, J = 6.8, 4.0, 3.2 Hz), 6.31 (1H, ddd, J = 8.2, 4.2, 4.0 Hz), 7.38–7.44 (6H, m), 7.48–7.51 (1H, m), 7.74–7.89 (3H, m), 7.90 (1H, d, J = 8.4 Hz), minor isomer δ 1.41 (1H, ddd, J = 12.5, 5.4, 3.5 Hz), 1.56 (3H, d, J = 6.9 Hz), 2.52 (1H, ddd, J = 12.9, 5.8, 2.3 Hz), 3.74 (1H, qdd, J = 6.8, 4.0, 3.2 Hz), 6.55 (1H, ddd, J = 11.6, 8.7, 5.7 Hz), 7.38–7.44 (6H, m), 7.48–7.51 (1H, m), 7.70 (1H, d, J = 8.4 Hz), 7.74–7.83 (3H, m); ^{13}C NMR ($CDCl_3$) δ 22.9 (q), 23.5 (q), 31.0 (q), 33.7 (q), 49.1 (d), 54.1 (d), 54.3 (d), 56.7 (d), 126.5 (d), 128.3 (d), 130.7 (d), 131.6 (d), 138.6 (s), 141.0 (s), 156.4 (s), 198.5 (s), 203.0 (s). Found: C, 65.97; H, 5.57; N, 8.56%. Calcd for $C_{18}H_{18}N_2S_2$: C, 66.22; H, 5.56; N, 8.58%.

22c (R^1 = *p*-$ClC_6H_4H_4$, R^2 = CH_3): Yellow crystals, mp 98.2–99.6 °C (dec.); MS *m/z* (%) 394 (M^+; 2), 223 ($M^+ - C_7H_6ClNS$; bp); IR (KBr) 3208, 2927, 1591, 1485, 1403, 1228, 1092, 1012, 940, 832, 753 cm^{-1}; ^1H NMR ($CDCl_3$) major-**22c**:minor-**22c** = 2:1, major isomer δ 1.53 (3H, d, J = 6.9 Hz), 1.76 (1H, ddd, J = 14.4, 10.6, 3.9 Hz), 2.31 (1H, ddd, J = 14.2, 3.9, 3.5 Hz), 3.71 (1H, qdd, J = 13.8, 10.3, 3.3 Hz), 6.26 (1H, ddd, J = 8.0, 4.1, 4.0 Hz), 7.26–7.37 (2H, m), 7.60–7.70 (2H, m), 7.73–7.77 (4H, m), minor isomer δ 1.44 (1H, ddd, J = 12.4, 12.4, 12.4 Hz), 1.56 (3H, d, J = 6.9 Hz), 2.49 (1H, ddd, J = 5.7, 2.9, 2.2 Hz), 3.63 (1H, qdd, J = 12.4, 12.4, 2.3 Hz), 6.50 (1H, ddd, J = 11.6, 8.7, 5.7 Hz), 7.26–7.37 (2H, m), 7.60–7.70 (2H, m), 7.73–7.77 (4H, m); ^{13}C NMR ($CDCl_3$) δ 22.9 (q), 23.5 (q), 30.9 (d), 31.5 (d), 33.6 (d), 49.3 (t), 54.2 (d), 54.5 (d), 57.0 (d), 90.1 (d), 128.0 (d), 128.2 (d), 128.6 (d), 128.8 (d), 136.6 (s), 136.9 (s), 139.0 (s), 139.1 (s), 155.4 (s), 157.4 (s), 197.1 (s), 197.9 (s). Found: C, 55.11; H, 4.08; N, 7.05%. Calcd for $C_{18}H_{16}Cl_2N_2S_2$: C, 54.68; H, 4.08; N, 7.09%.

23a (R^1 = C_6H_5, R^2 = CH_3): Red oil; MS *m/z* (%) 195 (M^+; 48), 64 (bp); IR (neat) 2925, 1624, 1476, 1443, 1368, 1256, 1089, 920, 765, 689 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.74 (3H, d, J = 6.4 Hz), 6.34 (1H, q, J = 9.6 Hz), 7.41–7.50 (5H, m). Found: C, 54.82; H, 4.41; N, 6.98%. Calcd for $C_9H_9NS_2$: C, 55.35; H, 4.64; N, 7.17%.

23b (R^1 = C_6H_5, R^2 = *t*-C_4H_9): Yellow oil; MS *m/z* (%) 237 (M^+; 2), 205 ($M^+ - S$, 5), 121 (bp); IR (neat) 2955, 1633, 1448, 1210, 1056, 1000, 766, 606 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.14 (9H, s), 6.32 (1H, s), 7.40–7.51 (3H, m), 7.83–7.85 (2H, m); ^{13}C NMR ($CDCl_3$) δ 26.7 (q), 38.9 (s), 104.1 (d), 128.7 (d), 129.0 (d), 131.7 (d), 132.1 (s), 165.1 (s). Found: C, 60.91; H, 6.56; N, 5.89%. Calcd for $C_{12}H_{15}NS_2$: C, 60.71; H, 6.37; N, 5.90%.

Thermal Reaction of 6*H*-1,3,5-Oxathiazines (5b). A toluene solution (20 ml) of 6*H*-1,3,5-oxathiazine (**5b**, 2.00 mmol) was heated at refluxing temperature for 3 h. After cooling to room temperature, the solvent was removed in vacuo. The crude product was then purified by using column chromatography on silica gel to afford a complex mixture including a small amount of a pair of diastereomers of **26b** and a trace amount of **23b** besides several unidentified products.

Major-26b (R^1 = C_6H_5, R^2 = *t*-C_4H_9): Yellow solid, mp 100.4–101.5 °C; MS *m/z* (%) 239 ($M^+ - C_{12}H_{16}NS$; 8), 205 ($M^+ - C_{12}H_{16}NS_2$; 98), 121 (bp); IR (neat) 3280, 2964, 1708, 1484, 1356, 1229, 770, 639 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.19 (18H, s), 5.86 (2H, d, J = 9.6 Hz), 7.36–7.48 (6H, m), 7.71–7.73 (4H, m), 8.09 (2H, d, J = 9.6 Hz); ^{13}C NMR ($CDCl_3$) δ 26.7 (q), 38.4 (s), 68.4 (d), 126.8 (d), 128.5 (d), 131.2 (d), 142.0 (s), 198.9 (s). Found: C, 64.22; H, 7.27; N, 6.26%. Calcd for $C_{24}H_{32}N_2S_3$: C, 64.82; H, 7.25; N, 6.30%.

Minor-26b (R^1 = C_6H_5, R^2 = *t*-C_4H_9): Yellow needles, mp 189.5–190.2 °C; MS *m/z* (%) 238 ($M^+ - C_{12}H_{15}NS$; 4), 205 ($M^+ - C_{12}H_{17}NS_2$; 98), 77 (bp); IR (neat) 3354, 2963, 1502, 1448, 1356, 1229, 776, 695 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.20 (18H, s), 6.20 (2H, d, J = 10.3 Hz), 7.22–7.27 (4H, m), 7.39–7.43 (6H, m), 8.14 (2H, br. d, J = 10.3 Hz); ^{13}C NMR ($CDCl_3$) δ 27.0 (q), 39.0 (s), 67.9 (d), 127.2 (d), 128.2 (d), 131.2 (d), 140.9 (s), 197.6 (s). Found: C, 64.30; H, 7.32; N, 6.56%. Calcd for $C_{24}H_{32}N_2S_3$: C, 64.82; H, 7.25; N, 6.30%.

Thermal Reaction of 6*H*-1,3,5-Oxathiazines (5a) in the Presence of Thiobenzamide. After a toluene solution (20 ml) of 6*H*-1,3,5-oxathiazine (**5a**, 420 mg, 2.00 mmol) was treated with thiobenzamide (**1a**, 274 mg, 2.00 mmol) in the presence or absence of $Et_2O{\cdot}BF_3$ (284 mg, 2.00 mmol), the reaction mixture was heated at refluxing temperature for 5 h. Then, after cooling the reaction mixture to room temperature, the reaction mixture was filtered to remove the unreacted thiobenzamide, and the solvent was removed in vacuo from the filtrate. The crude product was then purified by using column chromatography on silica gel to afford an epimeric mixture of **22a**, **23a**, and **24a**.

24a (R^1 = C_6H_5, R^2 = CH_3): Yellow oil; MS *m/z* (%) 266 (M^+; 93), 251 ($M^+ - CH_3$; 93), 225 (bp); IR (neat) 2975, 1601, 1571, 1524, 1489, 1447, 1316, 768, 690 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.74 (3H, d, J = 6.7 Hz), 5.01 (1H, q, J = 6.7 Hz), 7.43–7.54 (5H, m), 7.52–7.62 (1H, m), 8.21–8.23 (2H, m), 8.30–8.32 (2H, m); ^{13}C NMR ($CDCl_3$) δ 22.0 (q), 57.2 (s), 128.0 (d), 128.2 (d), 128.7 (d), 128.8 (d), 130.8 (d), 133.2 (d), 136.7 (s), 137.4 (s), 161.6 (s), 172.5 (s). Found: C, 71.99; H, 5.21; N, 10.07%. Calcd for $C_{16}H_{14}N_2S$: C, 72.15; H, 5.30; N, 10.25%.

Thermal Reaction of 6*H*-1,3,5-Oxathiazines (5b) in the Presence of Thioacetamide or Thiobenzamide (1a). After a toluene solution (30 ml) of 6*H*-1,3,5-oxathiazine (**5b**, 298 mg, 1.00 mmol) was treated with thioacetamide or thiobenzamide (**1a**, 1.00 mmol), the reaction mixture was heated at refluxing temperature for 5 h. Then, after cooling the reaction mixture to room temperature, the reaction mixture was filtered to remove the unreacted thioacetamide, and the solvent was removed in vacuo from the filtrate. The crude product was then purified by using column chromatography

on silica gel to afford an epimeric mixture of **26b** (major-**26b**:minor-**26b** = 5:3–5:4) and **23b** along with several unidentified products.

Thermal Reaction of 5,6-dihydro-4*H*-1,3,5-thiadiazine (21a). A toluene solution (30 ml) of 5,6-dihydro-4*H*-1,3-thiazine **21a** (195 mg, 0.60 mmol) was heated at refluxing temperature for 12 h. After cooling to room temperature, the solvent was removed in vacuo. The crude product was then purified by using column chromatography on silica gel to afford an epimeric mixture of **22a** (31 mg, 16%) besides the recovery of **21a** (131 mg, 73%).

Heating of 5,6-dihydro-4*H*-1,3,5-thiadiazine (21a) in the Presence of Dimethyl Acetylenedicarboxylate (DMAD). After a toluene solution (30 ml) of 5,6-dihydro-4*H*-1,3,5-thiadiazines **21a** (175 mg, 0.55 mmol) was treated with dimethyl acetylenedicarboxylate (DMAD, 1.549 g, 22 mmol), the reaction mixture was heated at refluxing temperature for 12 h. The reaction mixture was then cooled to room temperature, quenched with an aqueous NaOH solution, and extracted with dichloromethane. The organic layer was washed with water, and then dried over anhydrous Na_2SO_4 powder. After removing the solvent in vacuo, the crude product was purified by using column chromatography on silica gel to afford the cycloadduct **9a** (66 mg, 20%) besides the recovery of **21a** (137 mg, 78%).

Heating of 5,6-dihydro-4*H*-1,3,5-thiadiazine (21a) in the Presence of 2-Propanol. After a toluene solution (30 ml) of 5,6-dihydro-4*H*-1,3,5-thiadiazine (**21a**, 195 mg, 0.55 mmol) was treated with 2-propanol (10 ml, excess), the reaction mixture was heated at refluxing temperature for 8 h. Then, after cooling to room temperature and quenching with water, the reaction mixture was subjected to the usual workup. The crude product was purified by using column chromatography on silica gel to afford *N*-(1-isopropoxyethyl)thiobenzamide (**16a**, 83 mg, 34%) besides the recovery of **21a** (113 mg, 58%).

Thermal Reaction of 6*H*-1,3,5-Oxaselenazines (6). A benzene solution (20 ml) of 6*H*-1,3,5-oxaselenazine (**6**, 2.00 mmol) was heated at refluxing temperature for a several hours. After cooling to room temperature, the solvent was removed in vacuo. The crude product was then purified by using column chromatography on silica gel to afford 6*H*-1,3,5-selenadiazines **27**, 3H-1,2,4-diselenazoles **28**, epimeric mixtures of 2*H*-1,3-imidazolines, **29**, and selenoamides **30**.

27a ($R^1 = C_6H_5$, $R^2 = CH_3$): Yellow needles, mp 63.8–64.0 °C; MS *m/z* (%) 314 (M^+; 31, ^{80}Se), 273 (4), 211 (17), 169 (27), 104 (bp); IR (KBr) 3060, 2961, 2926, 2870, 1727, 1599, 1570, 1533, 1447, 1316, 1288, 1223, 1120, 924, 765, 706, 691, 673 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.89 (3H, d, J = 6.7 Hz), 5.13 (1H, q, J = 6.7 Hz), 7.44–7.61 (6H, m), 8.18–8.21 (2H, m), 8.28–8.31 (2H, m); ^{13}C NMR ($CDCl_3$) δ 23.0 (q), 56.5 (d), 128.0 (d), 128.2 (d), 128.7 (d), 129.5 (d), 130.8 (d), 133.1 (d), 136.9 (s), 139.2 (s), 163.5 (s), 174.0 (s); ^{77}Se NMR ($CDCl_3$) δ 235.0. Found: C, 61.47; H, 4.50; N, 8.91%. Calcd for $C_{16}H_{14}N_2Se$: C, 61.35; H, 4.50; N, 8.94%.

27b ($R^1 = C_6H_5$, $R^2 = t\text{-}C_4H_9$): Yellow oil; MS *m/z* (%) 356 (M^+; 34, ^{80}Se), 168 (bp); IR (neat) 2955, 1605, 1573, 1533, 1487, 1448, 1365, 1312, 1289, 1224, 1096, 943, 903, 762, 715, 689, 669, 657 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.22 (9H, s), 4.75 (1H, s), 7.43–7.57 (6H, m), 8.19–8.21 (2H, m), 8.32–8.35 (2H, m); ^{13}C NMR ($CDCl_3$) δ 27.6 (q), 36.4 (s), 74.1 (br. s), 128.06 (d), 128.12 (d), 128.7 (d), 129.5 (d), 130.6 (d), 132.9 (d), 137.1 (s), 139.4 (s), 163.3 (s), 174.7 (s). Found: C, 64.73; H, 5.80; N, 7.70%. Calcd for $C_{19}H_{20}N_2Se$: C, 64.22; H, 5.67; N, 7.88%.

27c ($R^1 = p\text{-}ClC_6H_4$, $R^2 = CH_3$): Yellow needles, mp 135.0–135.5 °C; MS *m/z* (%) 382 (M^+; 41, ^{80}Se, ^{35}Cl), 339 (6), 245 (14), 204 (39), 138 (52), 108 (bp); IR (neat) 3449, 1889, 1595, 1535, 1486, 833 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.86 (3H, d, J = 6.7 Hz), 5.11 (1H, q, J = 6.7 Hz), 7.38–7.41 (2H, m), 7.45–7.49 (2H, m), 8.06–8.09 (2H, m), 8.17–8.20 (2H, m); ^{13}C NMR ($CDCl_3$) δ 23.0 (q), 56.6 (s), 128.4 (d), 129.0 (d), 129.4 (d), 130.4 (d), 135.2 (s), 137.0 (s), 137.4 (s), 139.4 (s), 162.4 (s), 173.2 (s). Found: C, 50.19; H, 3.12; N, 6.96%. Calcd for $C_{16}H_{12}Cl_2N_2Se$: C, 50.29; H, 3.16; N, 7.33%.

28a ($R^1 = C_6H_5$, $R^2 = CH_3$): Red oil; MS *m/z* (%) 291 (M^+; bp, ^{80}Se), 188 (27), 160 (46), 132 (63), 108 (69); IR (neat) 3059, 2965, 2917, 1637, 1446, 1235, 1087, 891, 761, 688, 663, 586 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.90 (3H, d, J = 6.4 Hz), 6.64 (1H, q, J = 6.4 Hz), 7.19–7.55 (3H, m), 7.65–8.00 (2H, m); ^{13}C NMR ($CDCl_3$) δ 24.4 (q), 80.3 (d), 128.8 (d), 129.5 (d), 131.6 (d), 133.9 (s), 160.4 (s); ^{77}Se NMR ($CDCl_3$) δ 480.0 (d, J_{Se-Se} = 190 Hz), 568.0 (d, J_{Se-Se} = 190 Hz). Found: C, 37.58; H, 3.20; N, 4.69%. Calcd for $C_9H_9NSe_2$: C, 37.39; H, 3.14; N, 4.84%.

28b ($R^1 = C_6H_5$, $R^2 = t\text{-}C_4H_9$): Red oil; MS *m/z* (%) 333 (M^+; 99, ^{80}Se), 158 (bp); IR (neat) 2960, 1649, 1447, 1362, 1243, 1046, 894, 762, 688, 587 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.35 (9H, s), 6.66 (1H, s), 7.36–7.45 (3H, m), 7.78–7.80 (2H, m); ^{13}C NMR ($CDCl_3$) δ 27.3 (q), 38.7 (s), 101.1 (d), 128.6 (d), 129.3 (d), 131.4 (d), 134.1 (s), 159.2 (s). Found: C, 43.76; H, 4.59; N, 4.17%. Calcd for $C_{12}H_{15}NSe_2$: C, 43.52; H, 4.57; N, 4.23%.

28c ($R^1 = p\text{-}ClC_6H_4$, $R^2 = CH_3$): Red oil; MS *m/z* (%) 291 (M^+; bp, ^{80}Se); IR (neat) 3059, 2965, 2917, 1637, 1446, 1235, 1087, 891, 761, 688, 663, 586 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.89 (3H, d, J = 6.5 Hz), 6.62 (1H, q, J = 6.5 Hz), 7.37–7.41 (2H, m), 7.72–7.75 (2H, m); ^{13}C NMR ($CDCl_3$) δ 24.3 (q), 80.2 (d), 123.0 (d), 130.7 (d), 132.4 (s), 137.7 (s), 159.1 (s). Found: C, 33.36; H, 2.51; N, 4.21%. Calcd for $C_9H_8ClNSe_2$: C, 33.41; H, 2.49; N, 4.33%.

29a ($R^1 = C_6H_5$, $R^2 = CH_3$): Yellow crystals; MS *m/z* (%) 342 (M^+; 60, ^{80}Se), 300 ($M^+ - CH_3CH{=}N$; 19, ^{80}Se), 261 ($M^+ - SeH$; bp), 172 (M^+ – PhCHSe; 80), 169 (PhC=Se; 10, ^{80}Se), 117 (49); IR (neat) 3056, 2980, 2931, 1625, 1437, 1264, 1004, 739, 694 cm^{-1}; ^1H NMR ($CDCl_3$) major isomer δ 1.29 (3H, d, J = 6.4 Hz), 1.83 (3H, d, J = 6.4 Hz), 5.78 (1H, q, J = 6.4 Hz), 5.97 (1H, q, J = 6.4 Hz), 7.26–7.94 (10H, m), minor isomer δ 1.29 (3H, d, J = 6.4 Hz), 1.91 (3H, d, J = 6.4 Hz), 5.02 (1H, q, J = 6.4 Hz), 6.57 (1H, q, J = 6.4 Hz), 7.26–7.94 (10H, m); ^{13}C NMR ($CDCl_3$) δ 18.8 (q), 20.5 (q), 20.6 (q), 22.0 (q), 64.3 (d), 67.7 (d), 86.7 (d), 89.9 (d), 123.9 (d), 124.1 (d), 127.8 (d), 127.9 (d), 128.0 (d), 128.3 (d), 128.4 (d), 128.5 (d), 128.8 (d), 128.9 (d), 130.5 (s), 130.6 (s), 131.6 (d), 131.8 (d), 145.5 (s), 146.2 (s), 168.6 (s), 170.9 (s), 200.9 (s), 201.1 (s). Found: C, 63.44; H, 5.51; N, 7.80%. Calcd for $C_{18}H_{18}N_2Se$: C, 63.34; H, 5.32; N, 8.21%.

29c ($R^1 = p\text{-}ClC_6H_4$, $R^2 = CH_3$): Yellow oil; MS *m/z* (%) 410 (M^+; 27, ^{80}Se), 365 (8), 329 (19), 294 (14), 245 (bp), 206 (43), 165 (60), 137 (89), 108 (99), 73 (61); IR (neat) 2979, 2228, 1627, 1591, 1439, 1091, 833 cm^{-1}; ^1H NMR ($CDCl_3$) major isomer δ 1.30 (3H, d, J = 6.4 Hz), 1.80 (3H, d, J = 6.4 Hz), 5.74 (1H, q, J = 6.4 Hz), 5.89 (1H, q, J = 6.4 Hz), 7.21–7.83 (8H, m), minor isomer δ 1.30 (3H, d, J = 6.4 Hz), 1.88 (3H, d, J = 6.4 Hz), 4.93 (1H, q, J = 6.4 Hz), 6.53 (1H, q, J = 6.4 Hz), 7.23–7.67 (8H, m); ^{13}C NMR ($CDCl_3$) major isomer δ 18.7 (q), 22.1 (q), 67.7 (d), 86.8 (d), 125.6 (d), 128.6 (d), 129.0 (d), 129.2 (d), 129.3 (d), 135.4 (s), 135.4 (s), 138.9 (s), 144.7 (s), 169.9 (s), 170.9 (s), 199.6 (s), minor isomer δ 20.4 (q), 20.7 (q), 64.2 (s), 90.1 (d), 125.4 (d), 128.7 (d), 128.8 (d), 129.2 (d), 129.2 (d), 135.2 (s), 135.2 (s), 138.8 (s), 145.4 (s), 167.4 (s), 168.4 (s), 198.8 (s). Found: C, 52.90; H, 4.08; N, 6.48%. Calcd for $C_{18}H_{16}Cl_2N_2Se$: C, 52.71; H, 3.93; N, 6.83%.

30a ($R^1 = C_6H_5$, $R^2 = CH_3$): Yellow plates, mp 129.0–130.0

°C; MS *m/z* (%) 317 (M^+; 32, ^{80}Se), 236 (M^+ – Se; bp), 169 (43), 105 (24); IR (KBr) 3316, 1690, 1674, 1523, 1446, 1387, 971, 769, 699 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.71 (3H, d, J = 7.0 Hz), 6.29 (1H, quintet, J = 7.0 Hz), 7.38–7.69 (6H, m), 7.84–7.86 (2H, m), 8.07–8.09 (2H, m), 9.25 (1H, br. s); ^{13}C NMR ($CDCl_3$) δ 18.3 (q), 59.5 (d), 126.7 (d), 128.5 (d), 128.9 (d), 129.0 (d), 131.3 (d), 133.2 (s), 133.4 (d), 144.4 (s), 198.3 (s), 203.1 (s). Found: C, 60.48; H, 4.79; N, 4.41%. Calcd for $C_{16}H_{15}NOSe$: C, 60.76; H, 4.78; N, 4.43%.

30b (R^1 = C_6H_5, R^2 = *t*-C_4H_9): Yellow oil; MS *m/z* (%) 359 (M^+; 13, ^{80}Se), 104 (bp); IR (KBr) 3285, 2957, 1667, 1522, 1447, 1375, 1221, 736, 693, 684 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.08 (9H, s), 6.74 (1H, d, J = 9.6 Hz), 7.38–7.65 (6H, m), 7.76–7.81 (2H, m), 8.13–8.15 (2H, m), 8.75–8.77 (1H, m); ^{13}C NMR ($CDCl_3$) δ 27.4 (q), 37.0 (s), 68.9 (d), 126.7 (d), 128.6 (d), 128.9 (d), 129.0 (d), 131.2 (d), 133.9 (d), 137.6 (s), 145.2 (s), 201.1 (s), 205.7 (s). Found: C, 63.36; H, 5.93; N, 3.70%. Calcd for $C_{19}H_{21}NOSe$: C, 63.68; H, 5.91; N, 3.91%.

30c (R^1 = *p*-ClC_6H_4, R^2 = CH_3): Yellow plates, mp 157.0 –158.0 °C; MS *m/z* (%) 385 (M^+; 24, ^{80}Se, ^{35}Cl), 303 (M^+ – Se; bp), 203 (38), 139 (48%); IR (neat) 3265, 3029, 1671, 1590, 1529, 1485, 1404, 1229, 970, 737 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.69 (3H, d, J = 7.0 Hz), 6.21 (1H, dq, J = 8.0, 7.0 Hz), 7.36–7.38 (2H, m), 7.52–7.54 (2H, m), 7.77–7.79 (2H, m), 8.00–8.02 (2H, m), 9.14 (1H, br. s); ^{13}C NMR ($CDCl_3$) δ 18.3 (q), 59.6 (d), 128.0 (d), 128.8 (d), 129.0 (d), 129.5 (d), 130.3 (d), 131.5 (s), 137.7 (s), 141.2 (s), 142.6 (s), 197.1 (s), 201.7 (s). Found: C, 49.89; H, 3.40; N, 3.60%. Calcd for $C_{16}H_{13}Cl_2NOSe$: C, 49.90; H, 3.40; N, 3.64%.

Conversion of Selenoamide 30a into the Corresponding Amide 31a by Treating with *m*CPBA. To a dichloromethane solution (20 ml) of selenoamide **30a** (31 mg, 1.00 mmol) was added a dichloromethane solution of *m*CPBA (259 mg(80%), 1.20 mmol); the reaction mixture was stirred at –78 °C for 3 h. The reaction mixture was then quenched with an aqueous Na_2SO_3 solution, and extracted with dichloromethane. The organic layer was washed with an aqueous $NaHCO_3$ solution and with water, and then dried over anhydrous Na_2SO_4 powder. After removing the solvent in vacuo, the crude product was purified by using column chromatography on silica gel using chloroform as an eluent to give 2-amino-*N*-benzoylpropiophenone (**31a**, 16 mg, 63%).

31a (R^1 = C_6H_5, R^2 = CH_3): Colorless solid, mp 100.5–101.5 °C (Ref. 46–48, 104.0–105.0 °C); ^1H NMR ($CDCl_3$) δ 1.55 (3H, d, J = 7.0 Hz), 5.77 (1H, quintet, J = 7.0 Hz), 7.37–7.38 (1H, m), 7.44–8.06 (10H, m); ^{13}C NMR ($CDCl_3$) δ 19.9 (q), 50.5 (d), 127.0 (d), 128.5 (d), 128.7 (d), 128.9 (d), 131.6 (d), 133.7 (s), 134.0 (d), 134.1 (s), 166.5 (s), 199.1 (s). Found: C, 75.48; H, 5.79; N, 5.52%. Calcd for $C_{16}H_{15}NO_2$: C, 75.87; H, 5.97; N, 5.53%.

X-Ray Crystallographic Analysis of 27a. Single crystals with sizes of 0.25 × 0.20 × 0.4 mm were used for data collection on a Rigaku automated four-cycle diffractiometer (AFC5PR), equipped with a rotating anode (45 kV, 200 mA), using graphite-monochromated Mo $K\alpha$ radiation (λ = 0.71069 Å). The crystal data are as follows: a = 30.816(4), b = 10.524(2), c = 8.684(2) Å, β = 93.97(2)°, V = 2809.3(9) Å^3, the space group = C_2/c, Z = 8, D_{calcd} = 1.48 g cm^3, μ(Mo$K\alpha$) = 26.31 cm^{-1}. The 2θ-ω scan mode with a scan rate of 8° min^{-1} (ω) was employed with a scan range of (1.20 + 0.30tan θ). A total of 4305 reflections within 2θ = 60° were collected.

The structure was solved by a direct method and refined by a full-matrix least-squares method. All non-hydrogen atoms were refined anisotropically and hydrogen atoms found in the successive *D*-Fourier map were refined isotropically. In the crystal, there were mixed two isomers with two positions (equatorial and axial) in the methyl group of C(4). The occupancy ratio was about 65%:35% for two isomers with equatorial:axial positions. The final cycle of refinement was carried out using 1720 observed reflections within $I_o > 2.0\sigma(I_o)$ converged to the final $R = \sum||F_o| - |F_c||/\sum|F_o|$ value of 0.059 and $R_w = [\sum_w (|F_o| - |F_c|)^2/\sum_w F_o^2)]^{1/2}$ of 0.055. The maximum and minimum peaks on the final difference Fourier map correspond to 0.38 and –0.34 eÅ^{-3}, respectively.

Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, and the copies can be obtained on request, free of charge, by quoting the publication citation and the deposition number CCDC 154951. The data are also deposited as Document No. 74020 at the Office of the Editor of Bull. Chem. Soc. Jpn.

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