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 6H-1,3,5-oxathiazines or 6H-1,3,5-oxaselenazines, respectively, and the heterodienes were efficiently trapped by using acetylenic dienophiles. When 6H-1,3,5-oxathiazines or 6H-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 6H-1,3,5-oxathiazines or 6H-1,3,5-oxathiazines or 6H-1,3,5-oxathiazines 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 chalcogenand 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 H₂S, H₂Se, 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 heteroacetaltype 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 concern-



ing attempts to isolate or detect heterodienes ${\bf B}$ are also mentioned in this paper.

Results and Discussion

Preparation of 6H-1,3,5-Oxathiazines (5) and 6H-1,3,5-Oxaselenazines (6). 6H-1,3,5-Oxathiazines 5 and 6H-1,3,5oxaselenazines 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 Et₂O·BF₃ at room temperature according to reported methods.^{7,44} In all cases, the physical data of the products, including the MS, IR, ¹H NMR, and ¹³C 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 Et₂O·BF₃ 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**

| R ¹ /NH 1 (X=S) 2 (X=Se) | H ₂ | • (3) | $\begin{array}{c} R^{1} \xrightarrow{X} R^{2} \\ \xrightarrow{R^{2}} \\ 5 (X=S) \\ 6 (X=Se) \end{array}$ | | | |
|---|----------------|-------|--|---------------------------------|------------------|-------|
| Subst | rate | | $\text{Reagent} \ (3, 4)$ | Produ | ct ^{a)} | Yield |
| \mathbb{R}^1 | Х | 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 ₆ H ₄ | S | 1c | 3 (0.8) | CH ₃ | 5c | 38 |
| p-ClC ₆ H ₄ | S | 1c | 4 (2.4) | t-C ₄ H 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 ₆ H ₄ | Se | 2c | 3 (0.8) | CH ₃ | 6c | 53 |
| p-ClC ₆ H ₄ | Se | 2c | 4 (2.4) | t-C ₄ H 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 6H-1,3,5-Oxathiazines (5) or 6H-1,3,5-Oxaselenazines (6) in the Presence of an Acetylenic Dienophile, p-Benzoquinone, or Diethyl Azodicarboxylate (DEAD). А benzene or a toluene solution of 6H-1,3,5-oxathiazines 5 or 6H-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 4H-1,3-thiazine 9 or 4H-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 vields. 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 ¹H NMR spectra of **10a**, **12a**, and **12c** revealed longrange 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 6H-1,3,5-Oxathiazines (5) or 6H-1,3,5-Oxase-



Scheme 2.

| $\begin{array}{c} R^{1} \xrightarrow{X} R^{2} \\ R^{2} \\ R^{2} \\ R^{2} \\ \hline Solvent, Reflux \\ 6 (X=Se) \end{array} \xrightarrow{R^{4} (10 \text{ mol amt.})} \begin{array}{c} R^{1} \xrightarrow{X} \\ R^{2} \\ R^{2} \\ 7$ | | | | | | | | | 4 3) e) |
|--|---------------------------------|----|-----|--------------------|----------------------------|---------|------|--------------------------|---------------------|
| S | ubstrate | | | Dienophile | | Solvent | Time | Product | Yield ^{a)} |
| \mathbf{R}^1 | \mathbb{R}^2 | Х | 5,6 | R ³ | \mathbb{R}^4 | | /h | 9–12 | /% |
| C ₆ H ₅ | CH ₃ | S | 5a | CO ₂ Me | CO ₂ Me | Toluene | 1 | 9a | 85 |
| C_6H_5 | $t-C_4H_9$ | S | 5b | CO_2Me | $\rm CO_2Me$ | Toluene | 4 | 9b | 71 |
| C_6H_5 | CH_3 | S | 5a | CO_2Me | Н | Toluene | 3 | 10a | 42 |
| C_6H_5 | CH_3 | Se | 6a | CO_2Me | $\rm CO_2Me$ | Benzene | 2.5 | 11a | 78 |
| C_6H_5 | t-C ₄ H ₉ | Se | 6b | CO_2Me | $\mathrm{CO}_2\mathrm{Me}$ | Benzene | 2.5 | 11b ^{b)} | 53 |
| p-ClC ₆ H ₄ | CH_3 | Se | 6c | CO_2Me | CO_2Me | Benzene | 2.5 | 11c | 46 |
| C_6H_5 | CH_3 | Se | 6a | CO_2Me | Н | Benzene | 2.5 | 12a ^{c)} | 76 |
| p-ClC ₆ H ₄ | CH_3 | Se | 6c | CO_2Me | Н | Benzene | 2.5 | 12c ^{c)} | 33 |

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

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

| R1_ 5 6 | $(X=S) \\ (X=Se)$ | ł ² | | Nucleophile (exc Solvent, Reflu | R1 HN R ² 15, 16 (X=S) 17-20 (X=Se) | | | |
|-----------------------------------|-------------------|----------------|-----|--|--|------|-------------------|---------------------|
| S | ubstrate | | | Nucleophile | Solvent | Time | Product | Yield ^{a)} |
| \mathbb{R}^1 | \mathbb{R}^2 | Х | 5,6 | /Nu-H (excess) | | /h | 15-20 | /% |
| C ₆ H ₅ | CH ₃ | S | 5a | C ₂ H ₅ OH | C ₂ H ₅ OH | 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>i</i> -C ₃ H ₇ OH ^{c)} | Toluene | 4 | 16a | 95 |
| C_6H_5 | CH_3 | Se | 6a | CH ₃ OH | CH ₃ OH | 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 ₂ H ₅ OH | C_2H_5OH | 4 | 18b | 53 |
| p-ClC ₆ H ₄ | CH_3 | Se | 6c | CH ₃ OH | CH ₃ OH | 4 | 17c | 92 |
| p-ClC ₆ H 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 ₆ H ₅ CH ₂ SH ^{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 ¹H NMR and ¹³C NMR spectra of **21a** and **21c** measured in CDCl₃ at 27 °C showed rather complicated patterns with the broadening signals. However, the ¹H 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 $\delta = 1.77$ and 1.98 ppm for the major isomer and at $\delta = 1.71$ 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 ¹H NMR spectra of **21a** were also observed at $\delta = 5.60$ and 7.08 ppm for the major isomer and at $\delta = 5.88$ and 7.35 ppm for the minor isomer, respectively. The ¹³C NMR spectra of **21a** measured at -30 °C showed a couple of thiocarbonyl carbon signals at $\delta =$ 198.2 and 201.3 ppm along with the doublet signals at $\delta = 52.9$, 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 ¹³C 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 ¹H NMR and ¹³C 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, ¹H NMR, and ¹³C 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 ¹H 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 6H-1,3,5-Oxathiazine (5) in the Presence of a **Thioamide.** When a toluene solution of 6H-1,3,5-oxathiazine 5a was treated with 1.0 molar amount of thiobenzamide (1a) at refluxing temperature for 5 h, 6H-1,3,5-thiadiazine 24a was obtained in low yields along with an inseparable epimeric mixture of 4H-1,3-thiazines 22a; the treatment of a toluene solution of 5a with thiobenzamide (1a) in the presence of 1.0 molar amount of Et₂O·BF₃ 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 H₂S.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-

| | $P_{P_2}^{R^2}$ | <u>،</u> م | ∆► | R ¹ S. N R ¹ N R ¹ R ¹ 21 (R ² | γ R^2 N $12 S^2 S^2 CH_3)$ | $R^{1} + S$ $R^{2} + S$ | $H_{3}^{R^{1}} = \frac{R^{1}}{R^{2}}$ | + R ¹ H | $ \begin{array}{c} \mathbf{R}^{2} \mathbf{R}^{2} \mathbf{S} \\ \overset{\mathbf{N}}{\longrightarrow} \mathbf{N} \mathbf{R}^{1} \\ \mathbf{S} \left(\mathbf{R}^{2} = t C_{4} H_{9}\right) \end{array} $ | |
|-----------------------------------|-----------------|---------------|---------|---|--|---|---------------------------------------|--------------------|--|---|
| Sub | strate | | Solvent | Temp | Time | | Yields/% ^{a)} | | | |
| \mathbb{R}^1 | \mathbb{R}^2 | 5 | | | /h | 21 (major : minor) ^{b)} | 22 (isomeric ratio) ^{b)} | 23 | 26 | |
| C ₆ H ₅ | CH ₃ | 5a | Toluene | Reflux | 3 | 73 (21a , 4 : 1) | 22 (22a , 1 : 1) | trace (23a) | 0 (26a) | Ī |
| C_6H_5 | $t-C_4H_9$ | 5b | Toluene | Reflux | 5 | 0 | — | trace (23b) | trace (26b) ^{c)} | |
| p-ClC ₆ H ₄ | CH_3 | 5c | Toluene | Reflux | 5 | 49 (21c , 4 : 1) | 19 (22c , 1 : 1) | trace (23c) | 0 (26c) | |

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

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



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

a) Isolated yields. b) Estimated by integration of the ¹HNMR spectrum. c) The ratio of major-**26b** : minor-**26b** was estimated to be 5:3 by integration of the ¹HNMR spectrum of the diastereometric mixture.

mal Cycloreversion of 2H-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 6H-1,3,5-Oxaselenazines (6) in the Absence of Trapping Agents or in the Presence of a Dienophile. Heating of a benzene solution of 6H-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 6H-1,3,5-oxathiadines 5; in all cases 6H-1,3,5-selenadiazines 27, 3H-1,2,4-diselenazoles 28, an epimeric mixture of 2H-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 Et₂O·BF₃ 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, ¹H NMR, and ¹³C NMR spectra, and their elemental analysis data were also consistent with their structures. Especially, the ¹H NMR and ¹³C 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 ¹H NMR and ¹³C NMR also showed that **29** were isolated as epimeric mixtures (about 1:1 ratio estimated from the integration of the ¹H 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-1,3butadienes 8 as the similar formation route from 7 to 21. The structures of 30 were determined from their ¹H NMR and ¹³C 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 mCPBA (Scheme 4).49,50



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 ¹H NMR and ¹³C 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 hexanechloroform 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

| R ¹ N | Se R ² R ² 6 | 2 | $\begin{array}{c} \Delta \\ Ar \end{array} \xrightarrow{R_1} Se \\ N \\ R_1 \\ R_1 \\ 27 \end{array}$ | R ² R ⁻ + | Se N R ² 28 | e + | $R^{1} \rightarrow R^{2}$ $N \rightarrow R^{2}$ R^{2} 29 | R ¹ + | $R^{1} \xrightarrow{Se}_{O} R^{2} \xrightarrow{R^{2}}_{O} R^{1}$ | + R ¹ CSet | NH ₂ |
|-----------------------------------|--|----|---|------------------------------------|---------------------------------|------|--|-------------------|--|-----------------------|--------------------------------|
| Sub | strate | | Additive | Solvent | Temp | Time | | | Yields/% ^{a)} | | |
| \mathbb{R}^1 | \mathbb{R}^2 | 6 | (mol amt.) | | /°C | /h | 27 | 28 | 29 (major : minor) ^{b)} | 30 | 2 |
| C ₆ H 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 | <i>p</i> -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 ₆ H 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 ¹H 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-1,3butadienes 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 H₂S. 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 ¹H 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 6H-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-1,3butadienes 8 with p-tolunitrile,¹³ products 27–29 bearing ptolyl 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 2,3dimethyl-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. (Me₃Si)₂Se-Et₂O·BF₃;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 ¹H 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 6H-1,3,5-oxathiazines **5** and 6H-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. ¹H NMR spectra were recorded on a Bruker AC-400P (400 MHz) spectrometer, and the chemical shifts of the ¹H NMR spectra are given in δ relative to internal tetramethylsilane (TMS). ¹³C NMR spectra were recorded on a Bruker AC-400P (100 MHz). ⁷⁷Se 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 P₄O₁₀ and were freshly distilled before use. Benzene, toluene, and hexane were dried over CaH2 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 (Et₂O·BF₃), m-chloroperbenzoic acid (mCP-BA), elemental selenium, and sodium tetrahydroborate (NaBH₄) 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 (Me₃Si)₂Se (1.1 mol amt.) and Et₂O·BF₃ (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 NaHCO₃ solution, and extracted with dichloromethane. The organic layer was washed with water, and then dried over anhydrous Na₂SO₄ 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 ($\mathbf{R}^1 = \mathbf{C}_6 \mathbf{H}_5$): Yellow needles, mp 124.0–124.5 °C (Ref. 51, 126.0–126.5 °C).

2c ($\mathbf{R}^1 = \mathbf{p}$ -ClC₆ \mathbf{H}_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-4aryl-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 Et₂O-BF₃ (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 NaHCO₃ solution, and extracted with dichloromethane. The organic layer was washed with water, and then dried over an-hydrous Na₂SO₄ 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-oxathiazine (**5**) and **6d** was achieved by recrystallization using hexane-dichloromethane.

5a (**R**¹ = **C**₆**H**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; ¹H NMR (CDCl₃) 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); ¹³C NMR (CDCl₃) 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 C₁₁H₁₃NOS: C, 63.74; H, 6.32; N, 6.76%.

5b (**R**¹ = **C**₆**H**₅, **R**² = *t*-**C**₄**H**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; ¹H NMR (CDCl₃) 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); ¹³C NMR (CDCl₃) 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 C₁₇H₂₅NOS: C, 70.06; H, 8.65; N, 4.81%.

5c (**R**¹ = *p*-**ClC**₆**H**₄, **R**² = **CH**₃): Colorless needles, mp 101.9–102.5 °C (dec.); MS *m/z* (%) 197 (M⁺ – CH₃CHO; 17), 58 (bp); IR (KBr) 2979, 1606, 1489, 1398, 1311, 1238, 1230, 1162, 1089, 965, 846, 838, 827 cm⁻¹; ¹H NMR (CDCl₃) 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); ¹³C NMR (CDCl₃) 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 C₁₁H₁₂ClNOS: C, 54.66; H, 5.00; N, 5.79%.

5d ($\mathbf{R}^1 = p$ -ClC₆H₄, $\mathbf{R}^2 = t$ -C₄H₉): Colorless crystals, mp 95.4–96.0 °C (dec.); MS *m/z* (%) 325 (M⁺; 2), 268 (M⁺ – *t*-C₄H₉; 2), 239 (M⁺ – *t*-C₄H₉CHO; 17), 41 (bp); IR (KBr) 2954, 2866, 1611, 1479, 1229, 1063, 767, 691 cm⁻¹; ¹H NMR (CDCl₃) 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); ¹³C NMR (CDCl₃) 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 C₁₇H₂₄ClNOS: C, 62.65; H, 7.42; N, 4.30%.

6a ($\mathbf{R}^1 = \mathbf{C_6H_5}$, $\mathbf{R}^2 = \mathbf{CH_3}$):⁴⁴ Orange oil; MS m/z (%) 257 (M⁺; 50, ⁸⁰Se), 213 (bp); IR (neat) 3059, 2982, 2923, 1602, 1533, 1447, 1314, 1223, 1116, 951, 764, 691 cm⁻¹; ¹H NMR (CDCl₃) 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); ¹³C NMR (CDCl₃) 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 C₁₁H₁₃NOSe: C, 51.98; H, 5.15; N, 5.51%.

6b ($\mathbb{R}^1 = \mathbb{C}_6\mathbb{H}_5$, $\mathbb{R}^2 = t-\mathbb{C}_4\mathbb{H}_9$):⁴⁴ Pale yellow needles, mp 94.0–95.0 °C (Ref. 44, 98.0–98.5 °C); MS *m/z* (%) 252 ($\mathbb{M}^+ - t$ -BuCHO – 1; 14, ⁸⁰Se), 42 (bp); IR (neat) 2953, 1622, 1479, 1392, 1165, 1073, 1058, 999, 764, 694 cm⁻¹; ¹H NMR (CDCl₃) 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); ¹³C NMR (CDCl₃) 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 ($\mathbf{R}^1 = \mathbf{p}$ -ClC₆H₄, $\mathbf{R}^2 = CH_3$): Pale yellow needles, mp 88.7–89.1 °C; MS *m/z* (%) 245 (M⁺ – MeCHO; 79, ⁸⁰Se), 108 (bp); IR (KBr) 2976, 2921, 1607, 1487, 1397, 1225, 1163, 1089, 1058, 955, 828, 582 cm⁻¹; ¹H NMR (CDCl₃) 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); ¹³C NMR (CDCl₃) 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 C₁₁H₁₂ClNOSe: C, 45.77; H, 4.19; N, 4.85%.

Thermal Reaction of 6H-1,3,5-Oxathiazines (5) or 6H-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 6H-1,3,5-oxathiazine (5, 2.00 mmol) or 6H-1,3,5-oxaselenazine (6, 2.00 mmol) was treated with a trapping 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 Na₂SO₄ 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 ($\mathbf{R}^1 = \mathbf{C_6H_5}$, $\mathbf{R}^2 = \mathbf{CH_3}$, $\mathbf{R}^3 = \mathbf{R}^4 = \mathbf{CO_2CH_3}$): 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 (CDCl₃) 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); ¹³C NMR (CDCl₃) 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 C₁₅H₁₅NO₄S: C, 59.00; H, 4.95; N, 4.59%.

9b ($\mathbf{R}^1 = \mathbf{C_6H_5}$, $\mathbf{R}^2 = t \cdot \mathbf{C_4H_9}$, $\mathbf{R}^3 = \mathbf{R}^4 = \mathbf{CO_2CH_3}$): Colorless needles, mp 86.2–86.3 °C (dec.); MS *m/z* (%) 348 (M⁺ + 1; 2), 292 (M⁺ + 1 – C₄H₈; 55), 75 (bp); IR (neat) 3089, 2976, 1724, 1643, 1435, 1264, 1046, 992, 936, 767 cm⁻¹; ¹H NMR (CDCl₃) 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); ¹³C NMR (CDCl₃) 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 C₁₈H₂₁NO₄S: C, 62.23; H, 6.09; N, 4.03%.

10a ($\mathbf{R}^1 = \mathbf{C}_6 \mathbf{H}_5$, $\mathbf{R}^2 = \mathbf{C}\mathbf{H}_3$, $\mathbf{R}^3 = \mathbf{C}\mathbf{O}_2\mathbf{C}\mathbf{H}_3$, $\mathbf{R}^4 = \mathbf{H}$): 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 (CDCl₃) 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); ¹³C NMR (CDCl₃) 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 C₁₃H₁₃NO₂S: C, 63.13; H, 5.21; N, 5.62%.

11a ($\mathbf{R}^1 = \mathbf{C}_6\mathbf{H}_5$, $\mathbf{R}^2 = \mathbf{CH}_3$, $\mathbf{R}^3 = \mathbf{R}^4 = \mathbf{CO}_2\mathbf{CH}_3$): Yellow oil; MS *m/z* (%) 354 (M⁺ + 1; 13, ⁸⁰Se), 250 (bp), 218 (97); IR (neat) 2952, 1729, 1617, 1434, 1255, 765, 692 cm⁻¹; ¹H NMR (CDCl₃) 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); ¹³C NMR (CDCl₃) 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 C₁₅H₁₅NO₄Se: C, 51.15; H, 4.29; N, 3.98%.

11b ($\mathbf{R}^1 = \mathbf{C}_6\mathbf{H}_5$, $\mathbf{R}^2 = t-\mathbf{C}_4\mathbf{H}_9$, $\mathbf{R}^3 = \mathbf{R}^4 = \mathbf{CO}_2\mathbf{CH}_3$): Yellow oil; MS *m/z* (%) 316 ($\mathbf{M}^+ - \operatorname{Se} + 1$; bp); IR (neat) 3324, 2953, 1716, 1488, 1440, 1237, 1208, 1133, 1072, 763, 698 cm⁻¹; ¹H NMR (CDCl₃) 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); ¹³C NMR (CDCl₃) 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 CDCl₃ and a small amount of CD₃OD. 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 C₁₈H₂₁NO₄Se: C, 54.83; H, 5.37; N, 3.55%.

11c ($\mathbf{R}^1 = p$ -ClC₆H₄, $\mathbf{R}^2 = CH_3$, $\mathbf{R}^3 = \mathbf{R}^4 = CO_2CH_3$): Orange oil; MS *m/z* (%) 387 (M⁺; 5, ⁸⁰Se), 328 (11), 250 (84), 218 (bp); IR (neat) 2951, 1716, 1591, 1251, 834, 582 cm⁻¹; ¹H NMR (CDCl₃) 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); ¹³C NMR (CDCl₃) 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 C₁₅H₁₄ClNO₄Se: C, 46.59; H, 3.65; N, 3.62%.

12a ($\mathbf{R}^1 = \mathbf{C}_6\mathbf{H}_5$, $\mathbf{R}^2 = \mathbf{CH}_3$, $\mathbf{R}^3 = \mathbf{CO}_2\mathbf{CH}_3$, $\mathbf{R}^4 = \mathbf{H}$): Yellow oil; MS *m*/*z* (%) 296 (M⁺ + 1; 10, ⁸⁰Se), 192 (bp), 160 (32), 131 (37); IR (KBr) 2950, 1713, 1435, 1280, 1050, 910, 745, 651, 621 cm⁻¹; ¹H NMR (CDCl₃) 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); ¹³C NMR (CDCl₃) 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 C₁₃H₁₃NO₂Se: C, 53.07; H, 4.45; N, 4.76%.

12c ($\mathbf{R}^1 = p$ -ClC₆H₄, $\mathbf{R}^2 = CH_3$, $\mathbf{R}^3 = CO_2CH_3$, $\mathbf{R}^4 = H$): Orange oil; MS *m/z* (%) 329 (M⁺; 8, ⁸⁰Se), 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 (CDCl₃) 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); ¹³C NMR (CDCl₃) 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 C₁₃H₁₂ClNO₂Se: C, 47.51; H, 3.68; N, 4.26%.

13a ($\mathbf{R}^1 = \mathbf{C}_6 \mathbf{H}_5$, $\mathbf{R}^2 = \mathbf{C} \mathbf{H}_3$): Red needles, mp 126.0–127.0 °C; MS *m/z* (%) 317 (\mathbf{M}^+ ; 53, ⁸⁰Se), 212 (bp); IR (KBr) 3056, 1650, 1587, 1292, 889, 841, 770, 693 cm⁻¹; ¹H NMR (CDCl₃) 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); ¹³C NMR (CDCl₃) 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 C₁₅H₁₁NO₂Se: C, 56.97; H, 3.51; N, 4.43%.

14a ($\mathbf{R}^1 = \mathbf{C}_6 \mathbf{H}_5$, $\mathbf{R}^2 = \mathbf{C} \mathbf{H}_3$): Pale yellow oil; MS *m/z* (%) 385 (M⁺; 0.4, ⁸⁰Se), 43 (bp); IR (neat) 2984, 2936, 1733, 1713, 1627, 1447, 1374, 1283, 1091, 1039, 908, 764, 692, 592 cm⁻¹; ¹H NMR (CDCl₃) 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); ¹³C NMR (CDCl₃) 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 C₁₅H₁₉N₃O₄Se: 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**₆**H**₅, **R**² = *t*-**C**₄**H**₉, **Nu** = **OC**₂**H**₅): Yellow oil; MS m/z (%) 251 (M⁺; 50), 222 (M⁺ - C₂H₅; 84), 207 (M⁺ - OC₂H₅; 91), 87 (bp); IR (neat) 3397, 3290, 2963, 2904, 1501, 1481, 1449, 1370, 1362, 1116, 1069, 961, 736, 693 cm⁻¹; ¹H NMR (CDCl₃) 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); ¹³C NMR (CDCl₃) 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 C₁₄H₂₁NOS: C, 66.89; H, 8.42; N, 5.57%.

16a ($\mathbf{R}^1 = \mathbf{C}_6\mathbf{H}_5$, $\mathbf{R}^2 = \mathbf{CH}_3$, $\mathbf{Nu} = \mathbf{Oi}\cdot\mathbf{C}_3\mathbf{H}_7$): Yellow powder, mp 66.2–66.3 °C; MS m/z (%) 223 (\mathbf{M}^+ ; 5), 121 (bp); IR (KBr) 3253, 2976, 1710, 1519, 1447, 1379, 1245, 1109, 1086, 999, 965, 725, 697 cm⁻¹; ¹H NMR (CDCl₃) 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); ¹³C NMR (CDCl₃) 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 C₁₂H₁₇NOS: C, 64.53; H, 7.67; N, 6.27%.

17a ($\mathbf{R}^1 = \mathbf{C}_6 \mathbf{H}_5$, $\mathbf{R}^2 = \mathbf{CH}_3$, $\mathbf{Nu} = \mathbf{OCH}_3$): Yellow oil; MS *m/z* (%) 243 (M⁺; bp, ⁸⁰Se), 211 (M⁺ – CH₃OH; 64, ⁸⁰Se), 185 (83), 104 (95); IR (neat) 3211, 2989, 1510, 1449, 1378, 1131, 1093, 693 cm⁻¹; ¹H NMR (CDCl₃) 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); ¹³C NMR (CDCl₃) 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 C₁₀H₁₃NOSe: C, 49.60; H, 5.41; N, 5.78%.

18a ($\mathbf{R}^1 = \mathbf{C}_6\mathbf{H}_5$, $\mathbf{R}^2 = \mathbf{CH}_3$, $\mathbf{Nu} = \mathbf{OC}_2\mathbf{H}_5$): Yellow needles, mp 94.0–95.0 °C; MS m/z (%) 257 (M⁺; 11, ⁸⁰Se), 211 (M⁺ – C₂H₅OH; 15, ⁸⁰Se), 44 (bp); IR (KBr) 3241, 2980, 1510, 1483, 1448, 1231, 1113, 1087, 1054, 693, 675 cm⁻¹; ¹H NMR (CDCl₃) 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); ¹³C NMR (CDCl₃) 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 C₁₁H₁₅NOSe: C, 51.57; H, 5.90; N, 5.47%.

18b (**R**¹ = **C**₆**H**₅, **R**² = *t*-**C**₄**H**₉, **Nu** = **OC**₂**H**₅): Orange oil; MS *m/z* (%) 297 (M⁺; 12, ⁸⁰Se), 115 (bp); IR (neat) 3376, 3250, 2963, 1503, 1481, 1447, 1372, 1112, 1063, 695 cm⁻¹; ¹H NMR (CDCl₃) 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); ¹³C NMR (CDCl₃) 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 C₁₄H₂₁NOSe: C, 56.37; H, 7.10; N, 4.70%.

17c ($\mathbf{R}^1 = \mathbf{p}$ -CIC₆H₄, $\mathbf{R}^2 = CH_3$, Nu = OCH₃): Yellow needles, mp 101.0–102.0 °C; MS *m/z* (%) 277 (M⁺; 15, ⁸⁰Se), 246 (M⁺ – OCH₃; 10, ⁸⁰Se), 59 (bp); IR (KBr) 3254, 2988, 2930, 1588, 1510, 1481, 1399, 1372, 1238, 1132, 1086, 1039, 883, 822, 719 cm⁻¹; ¹H NMR (CDCl₃) 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); ¹³C NMR (CDCl₃) 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 $C_{10}H_{12}CINOSe: C$, 43.42; H, 4.37; N, 5.06%.

18c ($\mathbf{R}^1 = \mathbf{p}$ -CIC₆H₄, $\mathbf{R}^2 = CH_3$, Nu = OC₂H₅): Yellow needles, mp 85.0–86.0 °C; MS *m/z* (%) 289 (M⁺; 4, ⁸⁰Se), 246 (8), 44 (bp); IR (KBr) 3222, 2977, 1589, 1515, 1481, 1404, 1374, 1231, 1110, 1093, 1052, 932, 725 cm⁻¹; ¹H NMR (CDCl₃) 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); ¹³C NMR (CDCl₃) 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 C₁₁H₁₄CINOSe: 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 ($\mathbf{R}^1 = \mathbf{C}_6\mathbf{H}_5$, $\mathbf{R}^2 = \mathbf{CH}_3$, $\mathbf{Nu} = \mathbf{SC}_6\mathbf{H}_5$): Orange oil; MS m/z (%) 321 (\mathbf{M}^+ ; 2, ⁸⁰Se), 211 ($\mathbf{M}^+ - \mathbf{C}_6\mathbf{H}_5$ SH; 38, ⁸⁰Se), 66 (bp); IR (neat) 3210, 2979, 1583, 1483, 1447, 1361, 1246, 1124, 1025, 878, 765, 691, 570 cm⁻¹; ¹H NMR (CDCl₃) 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); ¹³C NMR (CDCl₃) 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 C₁₅H₁₅NSSe: C, 56.25; H, 4.72; N, 4.37%.

20a ($\mathbf{R}^1 = \mathbf{C}_6\mathbf{H}_5$, $\mathbf{R}^2 = \mathbf{CH}_3$, $\mathbf{Nu} = \mathbf{SCH}_2\mathbf{C}_6\mathbf{H}_5$): Red oil; MS *m/z* (%) 342 (M⁺; 37, ⁸⁰Se), 211 (M⁺ - C₆H₅CH₂SH; 38, ⁸⁰Se), 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 (CDCl₃) 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); ¹³C NMR (CDCl₃) 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 C₁₆H₁₇NSSe: 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 6H-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*-1,3thiazines **22**, 3*H*-1,2,4-dithiazoles **23**, and 6*H*-1,3,5-thiadiazines **24** besides several unidentified products.

21a ($\mathbf{R}^1 = \mathbf{C}_6 \mathbf{H}_5$, $\mathbf{R}^2 = \mathbf{C} \mathbf{H}_3$): Yellow oil; MS m/z (%) 265 (M⁺ - C₂H₆S; 3,), 205 (M⁺ - C₇H₅S; 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 (CDCl₃, -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); ¹³C NMR (CDCl₃, -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 C₁₈H₁₈N₂S₂: C, 66.22; H, 5.56; N, 8.58%.

21c (**R**¹ = *p*-**ClC**₆**H**₄, **R**² = **CH**₃): Yellow needles, mp 63.8–64.4 °C (dec.); MS *m/z* (%) 396 (M⁺; 1), 229 (M⁺ – C₉H₅ClS; 10) 196 (M⁺/2; bp); IR (KBr) 2985, 1714, 1621, 1592, 1488, 1399, 1091, 834 cm⁻¹; ¹H NMR (CDCl₃, –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); ¹³C NMR (CDCl₃, –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 C₁₈H₁₆Cl₂N₂S₂: C, 54.68; H, 4.08; N, 7.09%.

22a ($\mathbf{R}^1 = \mathbf{C}_6 \mathbf{H}_5$, $\mathbf{R}^2 = \mathbf{C} \mathbf{H}_3$): Yellow crystals, mp 178.1–179.5 °C (dec.); MS m/z (%) 326 (M⁺; 2), 294 (M⁺ - S; 1), 189 (M⁺ -C₆H₅CSN; bp); IR (KBr) 3265, 2968, 1705, 1606, 1448, 1362, 1229, 942, 768, 694 cm⁻¹; ¹H NMR (CDCl₃) 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 $\delta 1.41$ (1H, ddd, J = 12.5, 5.4, 3.5Hz), 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); $^{13}\mathrm{C}$ NMR (CDCl₃) δ 22.9 (q), 23.5 (q), 31.0 (g), 33.7 (g), 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 C₁₈H₁₈N₂S₂: C, 66.22; H, 5.56; N, 8.58%.

22c ($\mathbf{R}^1 = p$ -ClC₆H₄H₄, $\mathbf{R}^2 = CH_3$): Yellow crystals, mp 98.2-99.6 °C (dec.); MS m/z (%) 394 (M⁺; 2), 223 (M⁺ -C₇H₆ClNS; bp); IR (KBr) 3208, 2927, 1591, 1485, 1403, 1228, 1092, 1012, 940, 832, 753 cm⁻¹; ¹H NMR (CDCl₃) 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); ¹³C NMR (CDCl₃) 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 C₁₈H₁₆Cl₂N₂S₂: C, 54.68; H, 4.08; N, 7.09%.

23a ($\mathbf{R}^1 = \mathbf{C}_6 \mathbf{H}_5$, $\mathbf{R}^2 = \mathbf{C} \mathbf{H}_3$): Red oil; MS m/z (%) 195 (\mathbf{M}^+ ; 48), 64 (bp); IR (neat) 2925, 1624, 1476, 1443, 1368, 1256, 1089, 920, 765, 689 cm⁻¹; ¹H NMR (CDCl₃) 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 C₉H₉NS₂: C, 55.35; H, 4.64; N, 7.17%.

23b ($\mathbf{R}^1 = \mathbf{C}_6 \mathbf{H}_5$, $\mathbf{R}^2 = t \cdot \mathbf{C}_4 \mathbf{H}_9$): 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 (CDCl₃) δ 1.14 (9H, s), 6.32 (1H, s), 7.40–7.51 (3H, m), 7.83–7.85 (2H, m); ¹³C NMR (CDCl₃) 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 C₁₂H₁₅NS₂: C, 60.71; H, 6.37; N, 5.90%.

Thermal Reaction of 6H-1,3,5-Oxathiazines (5b). A toluene solution (20 ml) of 6H-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 ($\mathbb{R}^1 = \mathbb{C}_6\mathbb{H}_5$, $\mathbb{R}^2 = t-\mathbb{C}_4\mathbb{H}_9$): Yellow solid, mp 100.4–101.5 °C; MS *m*/*z* (%) 239 (M⁺ – $\mathbb{C}_{12}\mathbb{H}_{16}$ NS; 8), 205 (M⁺ – $\mathbb{C}_{12}\mathbb{H}_{16}$ NS₂; 98), 121 (bp); IR (neat) 3280, 2964, 1708, 1484, 1356, 1229, 770, 639 cm⁻¹; ¹H NMR (CDCl₃) 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); ¹³C NMR (CDCl₃) 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 $\mathbb{C}_{24}\mathbb{H}_{32}\mathbb{N}_2\mathbb{S}_3$; C, 64.82; H, 7.25; N, 6.30%.

Minor-26b ($\mathbb{R}^1 = \mathbb{C}_6\mathbb{H}_5$, $\mathbb{R}^2 = t-\mathbb{C}_4\mathbb{H}_9$): Yellow needles, mp 189.5–190.2 °C; MS *m/z* (%) 238 (M⁺ – $\mathbb{C}_{12}\mathbb{H}_{15}NS$; 4), 205 (M⁺ – $\mathbb{C}_{12}\mathbb{H}_{17}NS_2$; 98), 77 (bp); IR (neat) 3354, 2963, 1502, 1448, 1356, 1229, 776, 695 cm⁻¹; ¹H NMR (CDCl₃) 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); ¹³C NMR (CDCl₃) 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 $\mathbb{C}_{24}\mathbb{H}_{32}\mathbb{N}_2\mathbb{S}_3$: 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 -BF₃ (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 ($\mathbf{R}^1 = \mathbf{C}_6 \mathbf{H}_5$, $\mathbf{R}^2 = \mathbf{C} \mathbf{H}_3$): Yellow oil; MS m/z (%) 266 (M⁺; 93), 251 (M⁺ – CH₃; 93), 225 (bp); IR (neat) 2975, 1601, 1571, 1524, 1489, 1447, 1316, 768, 690 cm⁻¹; ¹H NMR (CDCl₃) 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); ¹³C NMR (CDCl₃) 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 C₁₆H₁₄N₂S: 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 Na₂SO₄ 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 6H-1,3,5-Oxaselenazines (6). A benzene solution (20 ml) of 6H-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 6H-1,3,5-selenadiazines **27**, 3H-1,2,4-diselenazoles **28**, epimeric mixtures of 2H-1,3-imidazolines, **29**, and selenoamides **30**.

27a ($\mathbf{R}^1 = \mathbf{C}_6 \mathbf{H}_5$, $\mathbf{R}^2 = \mathbf{C} \mathbf{H}_3$): Yellow needles, mp 63.8–64.0 °C; MS *m/z* (%) 314 (M⁺; 31, ⁸⁰Se), 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 (CDCl₃) 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); ¹³C NMR (CDCl₃) 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); ⁷⁷Se NMR (CDCl₃) δ 2350. Found: C, 61.47; H, 4.50; N, 8.91%. Calcd for C₁₆H₁₄N₂Se: C, 61.35; H, 4.50; N, 8.94%.

27b ($\mathbf{R}^1 = \mathbf{C}_6 \mathbf{H}_5$, $\mathbf{R}^2 = t \cdot \mathbf{C}_4 \mathbf{H}_9$): Yellow oil; MS m/z (%) 356 (M⁺; 34, ⁸⁰Se), 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 (CDCl₃) 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); ¹³C NMR (CDCl₃) 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 C₁₉H₂₀N₂Se: C, 64.22; H, 5.67; N, 7.88%.

27c ($\mathbf{R}^1 = \mathbf{p}$ -CIC₆H₄, $\mathbf{R}^2 = CH_3$): Yellow needles, mp 135.0–135.5 °C; MS *m/z* (%) 382 (M⁺; 41, ⁸⁰Se, ³⁵Cl), 339 (6), 245

(14), 204 (39), 138 (52), 108 (bp); IR (neat) 3449, 1889, 1595, 1535, 1486, 833 cm⁻¹; ¹H NMR (CDCl₃) 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); ¹³C NMR (CDCl₃) 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 C₁₆H₁₂Cl₂N₂Se: C, 50.29; H, 3.16; N, 7.33%.

28a (**R**¹ = **C**₆**H**₅, **R**² = **CH**₃): Red oil; MS m/z (%) 291 (M⁺; bp, ⁸⁰Se), 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 (CDCl₃) 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); ¹³C NMR (CDCl₃) δ 24.4 (q), 80.3 (d), 128.8 (d), 129.5 (d), 131.6 (d), 133.9 (s), 160.4 (s); ⁷⁷Se NMR (CDCl₃) 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 C₉H₉NSe₂: C, 37.39; H, 3.14; N, 4.84%.

28b ($\mathbf{R}^1 = \mathbf{C}_6\mathbf{H}_5$, $\mathbf{R}^2 = t \cdot \mathbf{C}_4\mathbf{H}_9$): Red oil; MS *m/z* (%) 333 (M⁺; 99, ⁸⁰Se), 158 (bp); IR (neat) 2960, 1649, 1447, 1362, 1243, 1046, 894, 762, 688, 587 cm⁻¹; ¹H NMR (CDCl₃) δ 1.35 (9H, s), 6.66 (1H, s), 7.36–7.45 (3H, m), 7.78–7.80 (2H, m); ¹³C NMR (CDCl₃) 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 C₁₂H₁₅NSe₂: C, 43.52; H, 4.57; N, 4.23%.

28c ($\mathbb{R}^1 = p$ -CIC₆H₄, $\mathbb{R}^2 = CH_3$): Red oil; MS m/z (%) 291 (M⁺; bp, ⁸⁰Se); IR (neat) 3059, 2965, 2917, 1637, 1446, 1235, 1087, 891, 761, 688, 663, 586 cm⁻¹; ¹H NMR (CDCl₃) 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); ¹³C NMR (CDCl₃) 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 C₉H₈CINSe₂: C, 33.41; H, 2.49; N, 4.33%.

29a ($\mathbf{R}^1 = \mathbf{C}_6\mathbf{H}_5$, $\mathbf{R}^2 = \mathbf{CH}_3$): Yellow crystals; MS *m/z* (%) 342 (M⁺; 60, ⁸⁰Se), 300 (M⁺ – CH₃CH=N; 19, ⁸⁰Se), 261 (M⁺ – SeH; bp), 172 (M⁺ – PhCHSe; 80), 169 (PhC=Se; 10, ⁸⁰Se), 117 (49); IR (neat) 3056, 2980, 2931, 1625, 1437, 1264, 1004, 739, 694 cm⁻¹; ¹H NMR (CDCl₃) 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); ¹³C NMR (CDCl₃) 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 C₁₈H₁₈N₂Se: C, 63.34; H, 5.32; N, 8.21%.

29c ($\mathbf{R}^1 = \mathbf{p}$ -CIC₆H₄, $\mathbf{R}^2 = CH_3$): Yellow oil; MS *m/z* (%) 410 (M⁺; 27, ⁸⁰Se), 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 (CDCl₃) 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); ¹³C NMR (CDCl₃) 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), 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 C₁₈H₁₆Cl₂N₂Se: C, 52.71; H, 3.93; N, 6.83%.

30a ($\mathbf{R}^1 = \mathbf{C}_6 \mathbf{H}_5$, $\mathbf{R}^2 = \mathbf{C} \mathbf{H}_3$): Yellow plates, mp 129.0–130.0

°C; MS m/z (%) 317 (M⁺; 32, ⁸⁰Se), 236 (M⁺ – Se; bp), 169 (43), 105 (24); IR (KBr) 3316, 1690, 1674, 1523, 1446, 1387, 971, 769, 699 cm⁻¹; ¹H NMR (CDCl₃) 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); ¹³C NMR (CDCl₃) 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 C₁₆H₁₅NOSe: C, 60.76; H, 4.78; N, 4.43%.

30b ($\mathbf{R}^1 = \mathbf{C}_6\mathbf{H}_5$, $\mathbf{R}^2 = t$ - $\mathbf{C}_4\mathbf{H}_9$): Yellow oil; MS m/z (%) 359 (M⁺; 13, ⁸⁰Se), 104 (bp); IR (KBr) 3285, 2957, 1667, 1522, 1447, 1375, 1221, 736, 693, 684 cm⁻¹; ¹H NMR (CDCl₃) 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); ¹³C NMR (CDCl₃) 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 C₁₉H₂₁NOSe: C, 63.68; H, 5.91; N, 3.91%.

30c ($\mathbf{R}^1 = \mathbf{p}$ -ClC₆H₄, $\mathbf{R}^2 = CH_3$): Yellow plates, mp 157.0 -158.0 °C; MS *m/z* (%) 385 (M⁺; 24, ⁸⁰Se, ³⁵Cl), 303 (M⁺ – Se; bp), 203 (38), 139 (48%); IR (neat) 3265, 3029, 1671, 1590, 1529, 1485, 1404, 1229, 970, 737 cm⁻¹; ¹H NMR (CDCl₃) 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); ¹³C NMR (CDCl₃) 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 C₁₆H₁₃Cl₂NOSe: 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 Na₂SO₃ solution, and extracted with dichloromethane. The organic layer was washed with an aqueous NaHCO₃ solution and with water, and then dried over anhydrous Na₂SO₄ 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 ($\mathbf{R}^1 = \mathbf{C}_6\mathbf{H}_5$, $\mathbf{R}^2 = \mathbf{CH}_3$): Colorless solid, mp 100.5–101.5 °C (Ref. 46–48, 104.0–105.0 °C); ¹H NMR (CDCl₃) 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); ¹³C NMR (CDCl₃) 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 C₁₆H₁₅NO₂: C, 75.87; H, 5.97; N, 5.53%.

X-Ray Crystallographic Analysis of 27a. Single crystals with sizes of $0.25 \times 0.20 \times 0.4$ 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 ($\lambda = 0.71069$ Å). The crystal data are as follows: a = 30.816(4), b = 10.524(2), c = 8.684(2) Å, $\beta = 93.97(2)^\circ$, V = 2809.3(9) Å³, the space group = C_2/c , Z = 8, $D_{calcd} = 1.48$ g cm³, μ (MoK α) = 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 $2\theta = 60^\circ$ 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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