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A Willgerodt–Kindler Type Selenation of Dihalomethane Derivatives, Chloroform, and Sodium Trichloroacetate by Treating with a Base, Elemental Selenium, and an Amine

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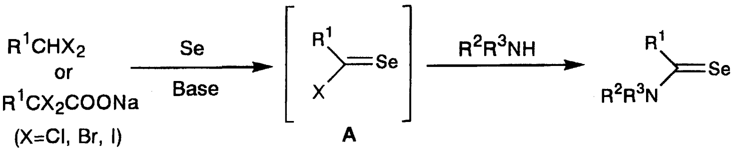
Treatment of dihalomethane derivatives, chloroform, or sodium trichloroacetate with elemental selenium in the presence of NaH and an excess amount of an amine gave the corresponding selenoamides, selenoureas, and bis(selenocarbamoyl) triselenides in modest yields. These products were afforded from reactive intermediates related to "selenocarbonyl halides" and "selenophosgenoids" generated by the reaction of dichloromethanide ions and trichloromethanide ion with *N*-alkylated aminopolyselenide species ($R_2N\text{–}(Se)_n{}^-$).

Recently, several methods have been reported for the conversion of carbonyl compounds to the corresponding selenocarbonyl compounds by the treatment with various selenating reagents possessing reactive metal–selenium bonds.[1—9] However, the syntheses of the selenocarbonyl compounds have often been impeded by the difficulty of the preparation and the treatment of such selenating reagents. Thus, current interests have been concentrated to the use of elemental selenium as the reagent to introduce the selenium functionalities into organic compounds.[10,11] Especially, in contrast to the extended works on the use of elemental sulfur for the syntheses of various thiocarbonyl compounds, fewer studies on the analogous synthetic use of elemental selenium have been reported except for the methods including the reactions of α-halo-substituted carbanions, carbenes, and carbenoids with elemental selenium.[12—14] During our studies on the synthetic use of elemental selenium for the convenient syntheses of selenocarbonyl compounds, we have expected that the reaction of dihalomethanide ions and trihalomethanide ion with activated elemental selenium would afford some reactive species related to hitherto unknown selenocarbonyl compounds such as "selenocarbonyl halides" and "selenophosgenoids", respectively. We have already reported the syntheses of selenoamides, selenoureas, and bis(selenocarbamoyl) triselenides (Scheme 1) by the treatment of dihalomethane derivatives, chloroform, or sodium trichloroacetate with a base, elemental selenium, and a secondary amine[15] under the reaction conditions conventionally used for the generation of α-halo- and α,α-dihalocarbenes from the substrates.[16,17] In this paper, we would like to describe the details of the novel selenation reactions of the substrates. The novel activation of elemental selenium with an amine, similar to the reaction of elemental sulfur with an amine in the well-known Willgerodt–Kindler reaction, is also described.[18]

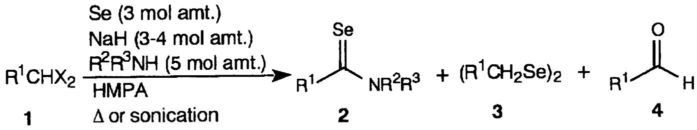
Results and Discussion

Reaction of Terminal *gem*-Dihaloalkanes with NaH, Elemental Selenium, and a Secondary Amine. To a HMPA solution of a dihalomethane was added NaH (3—4 mol amt.), elemental selenium (3 mol amt.), and an excess amount of diethylamine (5 mol amt.). The reaction mixture was heated at 120—130 °C for a few hours under an Ar atmosphere. After the usual workup and the chromatographic separation on silica gel, *N*,*N*-diethylselenoformamide (**2a**) was obtained in modest yield along with several by-products. Benzylidene dichlorides possessing various substituents were also converted into the corresponding selenoamides **2b**—**2f** in modest yields by similar treatments. The same reaction carried out at 80 °C in the presence of diethylamine predominantly afforded benzaldehyde (**4b**) along with a small amount of *N*,*N*-diethylselenobenzamide (**2b**) and dibenzyl diselenide (**3b**). The treatment of benzylidene dichloride with the reagents under the ultrasonic irradiation at room temperature also gave a similar result to that achieved at 80 °C in which **4b** was obtained as the major product. Indeed, benzaldehyde (**4b**) was mainly obtained by treating a HMPA solution of the starting substrate with NaH (3 mol amt.) and diethylamine (5 mol amt.) at 80 °C for 4 h or under ultra-



Scheme 1.

Table 1. Treatment of Dihalomethane Derivatives with NaH, Elemental Selenium, and a Primary or a Secondary Amine

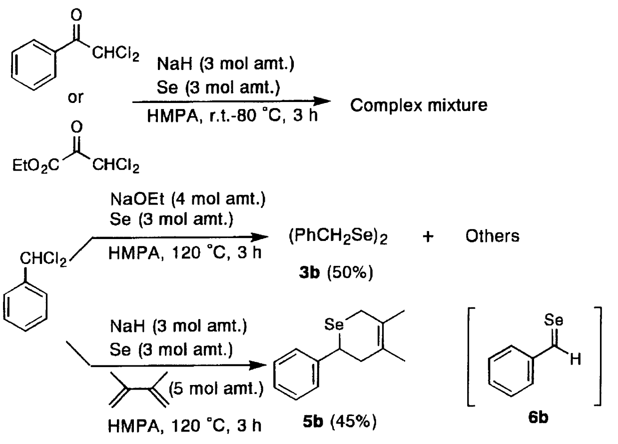


Substrate		Amine		Ultrasonic	Temp	Time	Yield/%[a]		
R^1	X	R^2	R^3	irradiation	°C	h	**2**	**3**	**4**
H	Cl	Et	Et	–	120	4	40 (**2a**)	—[b]	—[b]
H	Cl	Et	Et	+	R.T.	3	48 (**2a**)	—[b]	—[b]
H	Cl	*i*-Pr	*i*-Pr	+	R.T.	6	Complex mixture		
H	Br	Et	Et	–	130	3	47 (**2a**)	—[b]	—[b]
H	Br	Et	Et	+	R.T.	4	53 (**2a**)	—[b]	—[b]
H	I	Et	Et	–	120	3	48 (**2a**)	—[b]	—[b]
C_6H_5	Cl	Et	Et	–	120	3	41 (**2b**)	15 (**3b**)	trace
C_6H_5	Cl	Et	Et	–	80	6	3 (**2b**)	6 (**3b**)	50
C_6H_5	Cl	Et	Et	+	R.T.	3	6 (**2b**)	3 (**3b**)	75
C_6H_5	Cl	*i*-Pr	*i*-Pr	–	120	3	Complex mixture		
C_6H_5	Cl	Bu	H	–	120	3	10 (**2c**)	—[c]	—[c]
C_6H_5	Cl	$-(CH_2)_5-$		–	130	6	30 (**2d**)	8 (**3d**)	trace
p-$NO_2C_6H_4$	Cl	Et	Et	–	120	1	31 (**2e**)	10 (**3e**)	trace
p-$CH_3C_6H_4$	Cl	Et	Et	–	130	4	12 (**2f**)	—[c]	trace
C_6H_5CO	Cl	Et	Et	–	R.T.	5	80 (**2g**)	—[b]	—[b]
EtO_2C	Cl	Et	Et	–	80	4	40 (**2h**)[d]	—[b]	—[b]
EtO_2C	Cl	Et	Et	+	R.T.	2	51 (**2h**)	—[b]	—[b]

a) Isolated yields. b) Not detected. c) Not determined. d) A trace amount of *O*-Ethyl *N*,*N*-diethylselenocarbamate was obtained (2% yield) along with **2h**.

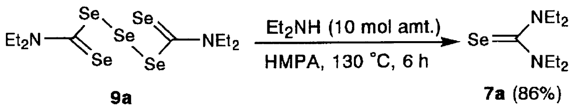
sonic irradiation at room temperature for 2 h in the absence of elemental selenium. It was assumed that the nucleophilic substitution of diethylamine toward the substrates occurred predominantly at lower temperature and the subsequent hydrolysis of the iminium intermediate during the usual workup gave aldehydes. Furthermore, the use of diisopropylamine for the reaction in place of diethylamine only gave a complex mixture in both cases, starting from dichloromethane and from benzylidene dichloride.

On the other hand, dichloromethane derivatives possessing an acidic proton at the carbon center were efficiently converted into the corresponding selenoamides **2g**—**2h** even at room temperature. In such cases ultrasonic irradiation was also effective for the acceleration of the selenation of dihalomethanes and sodium dichloroacetate. The structures of selenoamides **2** were confirmed by the spectral characterization and the identification with those of the reported physical data,[4,19,20] and the elemental analysis data, and were also supported by the selective conversion into the corresponding amides by treating with 1.2 molar amount of mCPBA at 0 °C.[21,22] Table 1 showed the results of the selenation reactions of various dihalomethane derivatives.



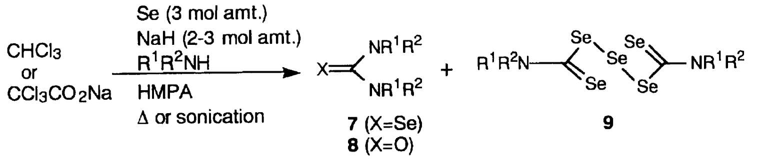
Scheme 2.

It is noteworthy that the use of DMF, DME, 1,4-dioxane, or acetonitrile as the solvent of the reactions in place of HMPA gave selenoamides **2** in rather low yields. The treatment of the substrates with elemental selenium and a secondary amine in the absence of NaH also gave discouraging results in all cases even if the reactions were carried out in HMPA. From several trials, we have found that more than 2 molar amount of NaH was necessary for the reactions. Indeed, dihalomethane derivatives possessing an acidic proton at the carbon center were converted into the corresponding selenoamides **2** at low temperature; the selenation of the substrates possessing low acidic protons required high reaction temperature. The use of NaH for the base of the reactions gave the best results among the bases including triethylamine,



Scheme 3.

Table 2. Treatment of Chloroform or Sodium Trichloroacetate with NaH, Elemental Selenium, and a Secondary Amine



Substrate	Amine		Ultrasonic	Temp	Time	Yield/% [a)]		
	R^1	R^2	irradiation	°C	h	**7**	**8**	**9**
$CHCl_3$ [b)]	Et	Et [c)]	–	130	3	37 (**7a**)	0	Trace
$CHCl_3$	Et	Et [c)]	–	R.T.	4	5 (**7a**)	0	46 (**9a**)
$CHCl_3$	Et	Et [c)]	+	R.T.	2	30 (**7a**)	0	13 (**9a**)
CCl_3CO_2Na	Et	Et [d)]	–	130	23	65 (**7a**)	23 (**8a**)	0
CCl_3CO_2Na	Et	Et [e)]	–	80	0.5	15 (**7a**)	trace	34 (**9a**)
CCl_3CO_2Na	Et	Et [c)]	+	R.T.	2	21 (**7a**)	—[f)]	16 (**9a**)
CCl_3CO_2Na	Bu	Bu [e)]	–	80	0.5	22 (**7b**)	—[f)]	35 (**9b**)
CCl_3CO_2Na	$-(CH_2)_5-$[e)]		–	100	1	43 (**7c**)	—[f)]	0

a) Isolated yields. b) *N*,*N*-Diethylselenoformamide **2a** was obtained in 13% yield besides selenourea **7a** ($R^1=R^2=Et$). c) 5 Molar amount of amine was used. d) 10 Molar amount of amine was used. e) 2.2 Molar amount of amine was used. f) Not determined.

DBU, *t*-BuOK, and Cs_2CO_3. However, the treatment of a HMPA solution of 2,2-dichloroacetophenone with NaH (3 mol amt.) and elemental selenium (3 mol amt.) at room temperature for 2 h in the absence of a secondary amine afforded a trace amount of a complex mixture in which no characterized compound was isolated. These results indicated that the combined use of NaH, elemental selenium, and an amine in HMPA was substantially necessary for the selenation reaction of these substrates.

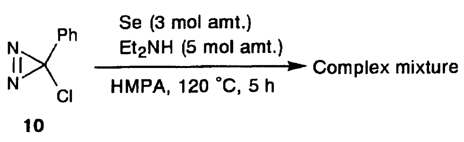
Interestingly, dibenzyl diselenide (**3b**) was obtained in 50% yield by a similar reaction of benzylidene dichloride carried out at 120 °C for 3 h in the absence of an amine (Scheme 2). A 3,6-dihydro-2-phenyl-4,5-dimethyl-2*H*-selenin (**5b**), the [4+2] cycloadduct of transiently generated selenobenzaldehyde (**6b**, $R^1 = Ph$) with 2,3-dimethyl-1,3-butadiene,[23)] was also given in 45% yield by this reaction performed in the presence of an excess amount of the diene. Segi has reported the generation and the trapping of selenoaldehydes by the treatment of dihalomethane derivatives possessing electron-withdrawing groups with selenide anion and Cs_2CO_3 in the presence of a diene.[24)] It was thus suggested that the competitive nucleophilic reaction of benzylidene dichloride with selenide anion species generated from elemental selenium and NaH in HMPA[25)] at about 120 °C afforded selenobenzaldehyde (**6b**, $R^1 = Ph$), which caused the further reduction to give the corresponding diselenide (**3b**).

Treatment of Chloroform or Sodium Trichloroacetate with NaH, Elemental Selenium, and an Excess Amount of a Secondary Amine. Treatment of a HMPA solution of chloroform with NaH (2—3 mol amt.), elemental selenium (3 mol amt.), and an excess amount of a secondary amine at 120—130 °C gave the corresponding selenourea **7** predominantly. When the reactions were performed in a similar manner using sodium trichloroacetate, NaH, and a secondary amine, the corresponding ureas **8** were given as main by-products besides selenoureas **7**, bis(*N*,*N*-dialkylselenocarbamoyl) triselenides **9**,[26,27)] and a trace amount of selenoformamide **2a**. On the other hand, when these reactions were performed at 80 °C, triselenides **9** were obtained predominantly. The same reactions of chloroform or sodium trichloroacetate performed under ultrasonic irradiation at room temperature also afforded **7** and **9** in modest yields. The structures of these products were confirmed by identification with those of the reported physical data,[19—21)] and the elemental analysis data. The conversion of selenoureas **7** into the corresponding ureas **8** was carried out efficiently by treating with mCPBA,[22,23)] and these results also supported the structures of **7**. Table 2 shows the results of the reactions.

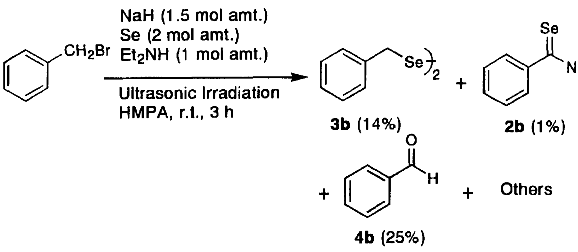
When a HMPA solution of bis(*N*,*N*-dimethylselenocarbamoyl) triselenide **9a** was treated with an excess amount of diethylamine at 130 °C according to the report of Henriksen,[19)] the corresponding selenourea **7a** was obtained in 86% yield (Scheme 3). This result suggested that triselenides **9** were formed as the primary products from some selenophosgene-like precursors in these reactions. The formation of *N*,*N*-diethylselenoformamide (**2a**) by the reaction of chloroform with NaH and elemental selenium in the presence of diethylamine at high temperature also suggested that the nucleophilic attack of in situ-generated selenide anion species to the carbon atom of chloroform was competing.[24)] In addition, ureas **8** were just obtained as minor products only in the case of the reaction starting from sodium trichloroacetate. The results indicated that ureas **8** originated from the reaction of the secondary amine with carbon dioxide generated by the decarboxylation of trichloroacetate ion.

On the other hand, the reaction of chloroform or sodium trichloroacetate with NaH and elemental selenium in the presence of a tertiary amine (triethylamine or DBU) afforded a trace amount of the unidentified products.

Plausible Reaction Path. Dihalomethane derivatives



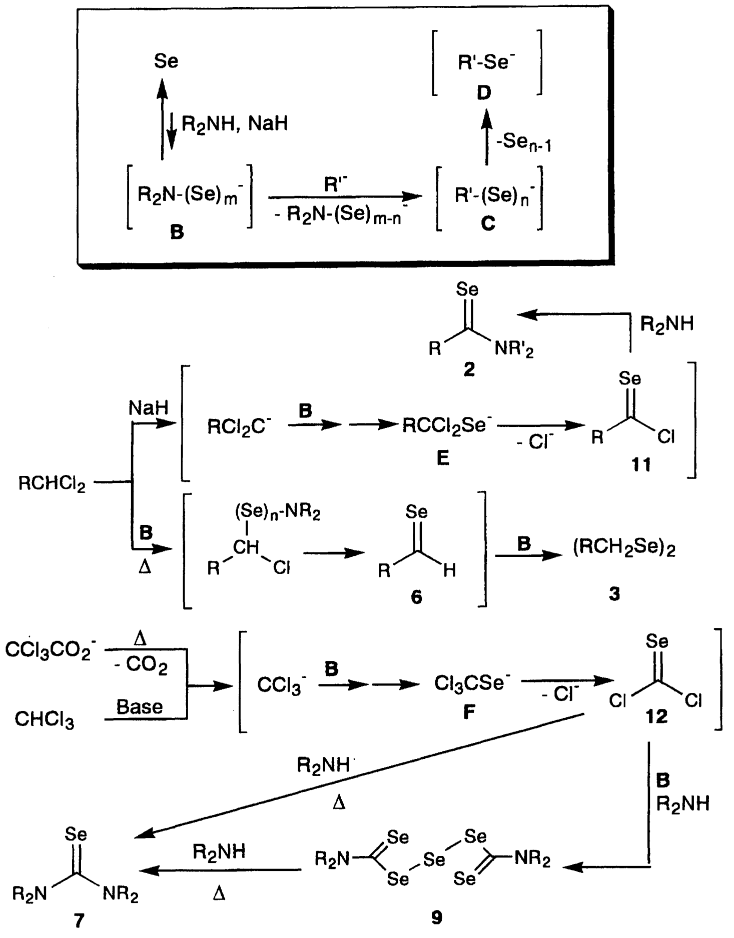
Scheme 4.



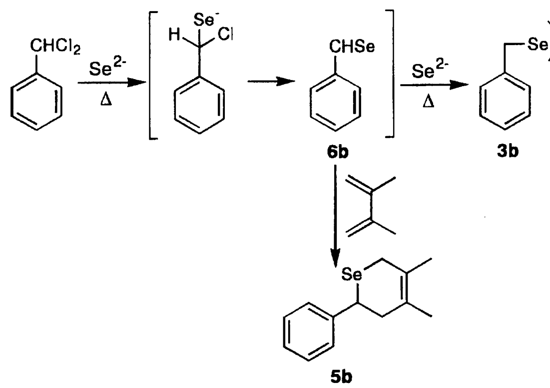
Scheme 5.

1 are known to generate α-halocarbenes by treating with a base,[17] and the carbene species are widely known to react with elemental sulfur and selenium to form thiones and selones, respectively. However, we have found that *N*,*N*-diethylselenobenzamide (**2b**) was not afforded at all by the thermal decomposition of 3-chloro-3-phenyldiazirine (**10**)[28—30] at 120 °C in the presence of elemental selenium and an excess amount of diethylamine as shown in Scheme 4. This result excluded the mechanism including the reaction of α-halocarbenes with elemental selenium. Thus, the alternative ionic mechanisms including the formation of dihalomethaneselenolate ions or trichloromethaneselenolate ion and the subsequent elimination of chloride ion from these species are postulated in the primary stage of these reactions.[18]

It is worth noting that the selenating reactions mentioned above required the combined use of elemental selenium with NaH and a primary or secondary amine in HMPA. This fact has strongly suggested that the reaction of elemental selenium with an amine in the presence of a base afforded a trace amount of some polyselenide ion species such as *N*-alkylated aminopolyselenide species **B**. When a HMPA solution of diethylamine (1 mol amt.) was treated with NaH (1 mol amt.) and elemental selenium (1 mol amt.) at room temperature under an Ar atmosphere, the color of the HMPA suspension of elemental selenium gradually turned into dark greenish brown. However, most elemental selenium remained insoluble in the reaction mixture even after the prolonged treatment. Such results suggested that only a trace amount of the activated selenium species (**B**) was generated in the equilibrated reaction mixture of a secondary amine, NaH, and elemental selenium. When the same reaction was carried out in DMF or DME, the color of the reaction mixture remained colorless to pale yellow. It is already known that various electron-transfer reactions are accelerated in a HMPA media. Thus, it is naturally assumed that the formation or the subsequent selenium



Scheme 6.



Scheme 7.

extrusion of *N*-alkylated aminopolyselenide species (**B**) may occur through a mechanism including the electron-transfer processes. Interestingly, when the greenish brown-colored HMPA suspension of elemental selenium, NaH, and diethylamine was treated with benzyl bromide (1 mol amt.) under ultrasonic irradiation at room temperature for 3 h, dibenzyl diselenide (**3b**, 14%) and a trace amount of *N*,*N*-diethylselenobenzamide (**2b**, 1%) were obtained along with benzaldehyde (**4b**, 25%) as shown in Scheme 5. This result was quite analogous to the Sato's results in which the reaction of benzyl chloride with elemental sulfur and a secondary amine also gave aldehyde **4b**, *N*,*N*-dialkylthiobenzamide, and dibenzyl disulfide in modest yields.[31] Sato has proposed that dibenzyl disulfide was afforded from *N*-alkylated aminodisulfide ion ($R_2N{-}S{-}S^-$) generated by the nucleophilic reaction of an amine with elemental sulfur.[18] Thus, the formation of diselenide **3b** was explained by the reaction of benzyl bromide with **B**, and **4b** was also produced by the nucleophilic attack of diethylamine with the substrate and the subsequent selenium-induced oxidation of the resulting benzylamine.[32,33] On the other hand, diisopropylamine was inert toward elemental selenium even in HMPA in the presence of NaH, and the treatment of dihalomethane derivatives with NaH, elemental selenium, and diisopropylamine only gave a complex mixture in which a trace amount of the corresponding selenoamides was found. Thus, our results suggested that a trace amount of *N*-alkylated aminopolyselenide species, $R_2N{-}(Se)_m^-$ (**B**), was initially formed in a HMPA media by the nucleophilic attack of amine or amide anion to elemental selenium. Furthermore, the activated selenium species (**B**) were also thought to behave not only as the substantial selenating agent toward carbanions to generate alkaneselenolate ions **D** via the formation and the subsequent selenium-extrusion of alkanepolyselenolate ions **C** in the primary stage of the selenation process but also as novel selenium nucleophiles toward the substrates. It was also assumed that the ultrasonic irradiation affected not only for the reaction of a dihalomethane with a base to generate α-halocarbanion but also for the acceleration of the nucleophilic attack of an amine to HMPA-insoluble elemental selenium to form **B**.[34]

Dichloromethanide ions and trichloromethanide ion generated from the substrates were thought to react with **B** to give the corresponding reactive species related to selenocarbonyl halides **11** and selenophosgene (**12**),[35] respectively, through the formation of ionic intermediates, such as dichloromethaneselenolate ions **E** and trichloromethaneselenolate ion **F**, and the subsequent elimination of chloride ion from **E** and **F**.[14,36] The intermediates, **11** and **12**, were thus converted into the corresponding selenoamides **2** and selenoureas **7** by the subsequent nucleophilic attack of the amine in the reaction mixture, as shown in Scheme 6. Dibenzyl diselenide (**3b**) was also formed by the competitive nucleophilic attack of **B** toward the carbon center of benzylidene dichloride and the subsequent further reduction of selenobenzaldehyde (**6b**) by the reaction with **B**. Selenoaldehyde **6b** was also formed by the nucleophilic attack of selenide ion (Se^{2-}) to benzylidene dichloride at a much higher temperature even in the absence of diethylamine (Scheme 7).[24] It was assumed that the similar nucleophilic attack of **B** to the carbon center of chloroform also generated some reactive species related to "selenoformyl chloride", which might react with diethylamine to give a small amount of *N*,*N*-diethylselenoformamide (**2a**). However, in all cases, no products originating from the selenolate ion intermediates, such as diselenides $RCCl_2Se{-}SeCCl_2R$ or $CCl_3Se{-}SeCCl_3$, were found in the crude reaction mixture, and all attempts to trap or detect the intermediates such as **B**, **C**, **D**, **E**, **F**, **11**, and **12** were not successful.

Conclusion. This work has provided a convenient synthesis of selenoamides and selenoureas by using a Willgerodt–Kindler type selenation of dihalomethane derivatives, chloroform, and sodium trichloroacetate. Further studies on the synthetic application and the mechanistic investigations of these reactions including the trapping or detecting the intermediates are in progress in our laboratory.

Experimental

Instruments. Melting points were determined with a Büchi 535 micro melting point apparatus. ^{1}H NMR spectra were recorded on a Hitachi R-90 (90 MHz) or a Bruker AC-400P (400 MHz) spectrometer. The chemical shifts of the ^{1}H NMR spectra are given in δ relative to internal tetramethylsilane (TMS). 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 by using a Yanagimoto MT-3 CHN Analyzer. The ultrasonic irradiation was performed by a Kaiji Denki Sono Cleaner 100A.

Materials. Column chromatography was performed by using Merck silica gel (Cat. No. 7734) without pretreatment. Dichloromethane and chloroform were dried over P_4O_{10} and were freshly distilled before use. Benzene and hexane were dried over CaH_2 and were freshly distilled before use. DME, 1,4-dioxane, and diethyl ether were pretreated with sodium metal, and were dried over $LiAlH_4$ and were freshly distilled before use. Hexamethylphosphoric triamide (HMPA), *N*,*N*-dimethylformamide (DMF), acetonitrile, ethanol, dimethyl sulfoxide (DMSO), diethylamine, piperidine, butylamine, and dibutylamine were dried over Merck Molecular Sieves 0.3 nm (Ca. No. 1.05704) and were freshly distilled before use. All substrates and reagents including sodium hydride, elemental selenium, benzylidene dichloride, dibromomethane, diiodomethane, phosphorus pentachloride, *p*-tolualdehyde, *p*-nitrobenzaldehyde, acetophenone, *m*-chloroperbenzoic acid (mCPBA), benzamidine hydrochloride, lithium chloride, aqueous sodium hypochlorite solution, and 2,3-dimethyl-1,3-butadiene were commercially available reagent grade and were used without any pretreatment.

A Typical Procedure for the Preparation of 4-Substituted Benzylidene Dichlorides.[37] Powdered phosphorus pentachloride (4.58 g, 22.0 mmol) was added dropwise to a dichloromethane solution of *p*-nitrobenzaldehyde (3.02 g, 20.0 mmol) at 0 °C, and the reaction mixture was stirred for 2 h. The reaction was quenched with an excess amount of water, and the reaction mixture was extracted with dichloromethane. The organic layer was washed with an aqueous $NaHCO_3$ solution and with water, and was dried over anhydrous Na_2SO_4 powder. The solvent was removed by evaporation and the residual solid was recrystallized with ethanol to give *p*-nitrophenyldichloromethane (3.07 g, 75%) as pale yellow needles.

A Typical Procedure of the Reaction of Dihalomethanes, Aryldihalomethanes, 2,2-Dichloroacetophenone, or Ethyl Dichloroacetate with NaH, Elemental Selenium, and a Secondary Amine. A 10 ml HMPA solution of a mixture of the substrate (6 mmol) and diethylamine (2.19 g, 30.0 mmol) was added to a HMPA suspension of NaH (720 mg (60% in oil), 18.0 mmol) and elemental selenium (1.42 g, 18.0 mmol), and the reaction mixture was stirred at the ambient temperature for 3 h under an Ar atmosphere. The reaction was quenched with an excess amount of water, and the reaction mixture was filtered off to remove the unreacted selenium. The filtrate was extracted with benzene. The organic layer was washed with water and with brine, and was dried over anhydrous Na_2SO_4 powder. The solvent was removed by evaporation and the residue was separated by column chromatography on silica gel using hexane–diethyl ether as an eluent to give the corresponding selenoformamide **2** in modest yields.

A Typical Procedure of the Reaction of Dihalomethanes or Aryldichloromethanes with NaH, Elemental Selenium, and a Secondary Amine under Ultrasonic Irradiation. A 10 ml HMPA solution of a mixture of a dihalomethane or an aryldihalomethane (3.00 mmol) and diethylamine (1.10 g, 15.0 mmol) was added to a HMPA suspension of NaH (360 mg (60% in oil), 9.00 mmol) and elemental selenium (711 mg, 9.00 mmol), and the reaction mixture was subjected to ultrasonic irradiation at room temperature for 3—4 h under an Ar atmosphere. The reaction was quenched with an excess amount of water, and the reaction mixture was subjected to the usual workup to give the corresponding selenoamide **2** in modest yields.

Procedure of the Reaction of Benzylidene Dichloride with NaH and Elemental Selenium. A 10 ml HMPA solution of a mixture of benzylidene dichloride (480 mg, 2.98 mmol) was added to a 5 ml ethanolic suspension of elemental selenium (706 mg, 8.94 mmol) and NaH (476 mg (60% in oil), 11.9 mmol), and the reaction mixture was stirred at 120 °C for 3 h under an Ar atmosphere. The reaction was quenched with an excess amount of water, and the reaction mixture was subjected to the usual workup to give dibenzyl diselenide (**3b**, 254 mg, 50%) as yellow needles.

Procedure of the Reaction of Benzylidene Dichloride with NaH and Elemental Selenium in the Presence of 2,3-Dimethyl-1,3-butadiene. A 10 ml HMPA solution of a mixture of benzylidene dichloride (480 mg, 2.98 mmol) and 2,3-dimethyl-1,3-butadiene (1.22 g, 14.9 mmol) was added to a HMPA suspension of NaH (476 mg (60% in oil), 11.9 mmol) and elemental selenium (706 mg, 8.94 mmol), and the reaction mixture was stirred at 120 °C for 3 h under an Ar atmosphere. The reaction was quenched with an excess amount of water, and the reaction mixture was subjected to the usual workup to give 3,6-dihydro-2-phenyl-4,5-dimethyl-2*H*-selenin (**5b**, 337 mg, 45%)[23] as a pale yellow oil.

Preparation of 3-Chloro-3-phenyldiazirine (10).[38] A DMSO–hexane solution (1 : 1) of lithium chloride was treated with benzamidine hydrochloride (2.35 g, 15.0 mmol) and with aqueous sodium hypochlorite solution (200 ml) at 0 °C, and the reaction mixture was stirred for 20 min. The reaction was quenched with an excess amount of water, and the reaction mixture was extracted with diethyl ether. The organic layer was washed with water, and was dried over anhydrous Na_2SO_4 powder. The solvent was removed and the residue was separated by column chromatography on silica gel using hexane–diethyl ether as an eluent to give 3-chloro-3-phenyldiazirine (**10**, 834 mg, 37%) as a colorless oil.

Thermal Decomposition of 3-Chloro-3-phenyldiazirine in the Presence of Elemental Selenium and an Excess Amount of Diethylamine. To a HMPA solution of freshly prepared 3-chloro-3-phenyldiazirine (**10**, 458 mg, 3.00 mmol) was added elemental selenium (711 mg, 9.00 mmol) and diethylamine (1.10 g, 15.0 mmol), and the reaction mixture was heated at 120 °C for 5 h. The reaction mixture was cooled to room temperature. An excess amount of water was added to quench the reaction, and the mixture was subjected to the usual workup. However, no identifiable compounds including *N,N*-diethylselenobenzamide (**2b**) were found in the resulting complex mixture.

Physical Data of 2. 2a (R^1=H, R^2=R^3=Et): Pale yellow oil; MS (*m/z*) 165 (M^+; bp, ^{80}Se); IR (neat) 2976, 1516 cm^{-1}; ^1H NMR ($CDCl_3$) $\delta = 1.30$ (3H, t, $J = 7.6$ Hz), 1.32 (3H, t, $J = 7.6$ Hz), 3.56 (2H, q, $J = 7.6$ Hz), 3.95 (2H, q, $J = 7.6$ Hz), 10.64 (1H, s). Found: C, 36.41; H, 6.91; N, 8.37%. Calcd for $C_5H_{11}NSe$: C, 36.59; H, 6.76; N, 8.54%.

2b (R^1=C_6H_5, R^2=R^3=Et): Yellow needles, mp 56.5—57.5 °C (lit.[21] 53.5—54.5 °C).

2c (R^1=Ph, R^2=Bu, R^3=H): Yellow oil; MS (*m/z*) 241 (M^+; bp, ^{80}Se); IR (neat) 3205, 2958, 1531 cm^{-1}; ^1H NMR ($CDCl_3$) $\delta = 0.95$—1.90 (7H, m), 3.76 (2H, dt, $J = 7.0$, 6.0 Hz), 7.27—7.74 (5H, m), 8.00—8.26 (1H, m). Found: C, 55.10; H, 6.58; N, 5.73%. Calcd for $C_{11}H_{15}NSe$: C, 55.00; H, 6.29; N, 5.83%.

2d (R^1=Ph, R^2=R^3=$-(CH_2)_5-$): Red prisms, mp 88—89 °C (lit,[20] 89—89.5 °C).

2e (R^1=*p*-$NO_2C_6H_4$, R^2=R^3=Et): Orange prisms, mp 143—144 °C; MS (*m/z*) 286 (M^+; bp, ^{80}Se); IR (KBr) 2976, 1589, 1519, 1490, 1344, 852 cm^{-1}; ^1H NMR ($CDCl_3$) $\delta = 1.19$ (3H, t, $J = 7.0$ Hz), 1.47 (3H, t, $J = 7.0$ Hz), 3.45 (2H, q, $J = 7.0$ Hz), 4.26 (2H, q, $J = 7.0$ Hz), 7.36 (2H, br.d, $J = 8.0$ Hz), 8.25 (2H, br.d, $J = 8.0$ Hz). Found: C, 46.28; H, 4.80; N, 9.72%. Calcd for $C_{11}H_{14}N_2O_2Se$: C, 46.33; H, 4.95; N, 9.82%.

2f (R^1=*p*-$CH_3C_6H_4$, R^2=R^3=Et): Yellow prisms, mp 97—97.5 °C; MS (*m/z*) 255 (M^+; 69%, ^{80}Se); IR (KBr) 2977, 1514, 1358, 810 cm^{-1}; ^1H NMR ($CDCl_3$) $\delta = 1.15$ (3H, t, $J = 7.0$ Hz), 1.44 (3H, t, $J = 7.0$ Hz), 2.33 (3H, s), 3.46 (2H, q, $J = 7.0$ Hz), 4.25 (2H, q, $J = 7.0$ Hz), 7.13 (4H, br.s). Found: C, 56.62; H, 6.77; N, 5.29%. Calcd for $C_{12}H_{17}NSe$: C, 56.69; H, 6.74; N, 5.51%.

2g (R^1=C_6H_5CO, R^2=R^3=Et): Orange oil; MS (*m/z*) 269 (M^+; 75%, ^{80}Se); IR (neat) 2979, 1660, 1596, 1580, 1519, 697 cm^{-1}; ^1H NMR ($CDCl_3$) $\delta = 1.22$ (3H, t, $J = 7.0$ Hz), 1.46 (3H, t, $J = 7.0$ Hz), 3.50 (2H, q, $J = 7.0$ Hz), 4.17 (2H, q, $J = 7.0$ Hz), 7.20—8.10 (5H, m). Found: C, 53.47; H, 5.63; N, 5.00%. Calcd for $C_{12}H_{15}NOSe$: C, 53.74; H, 5.64; N, 5.22%.

2h (R^1=CO_2Et, R^2=R^3=Et): Orange oil; MS (*m/z*) 237 (M^+; bp, ^{80}Se); IR (neat) 2981, 1725, 1519 cm^{-1}; ^1H NMR ($CDCl_3$) $\delta = 1.34$ (3H, t, $J = 7.0$ Hz), 1.36 (3H, t, $J = 7.0$ Hz), 1.38 (3H, t, $J = 7.0$ Hz), 3.52 (2H, q, $J = 7.0$ Hz), 4.01 (2H, q, $J = 7.0$ Hz), 4.38

(2H, q, $J=7.0$ Hz). Found: C, 40.55; H, 6.45; N, 5.70%. Calcd for $C_8H_{15}NO_2Se$: C, 40.69; H, 6.40; N, 5.93%.

Reaction of Sodium Trichloroacetate with NaH, Elemental Selenium, and Diethylamine. A 10 ml HMPA suspension of a mixture of sodium trichloroacetate (927 mg, 5.00 mmol), NaH (400 mg (60% in oil), 10.0 mmol), elemental selenium (1.184 g, 15.0 mmol), and diethylamine (805 mg, 11.0 mmol) was stirred at 80 °C for 30 min. The reaction mixture was quenched with an excess amount of water and the reaction mixture was filtered off to remove the unreacted selenium. The filtrate was extracted with benzene. The organic layer was washed with water and with brine, and was dried over anhydrous Na_2SO_4 powder. The solvent was removed and the brown residue was separated by column chromatography on silica gel using benzene–chloroform as an eluent to give *N*,*N*,*N*′,*N*′-tetraethylselenourea (**7a**, 178 mg, 15%), bis(*N*,*N*-diethylselenocarbamoyl) triselenide (**9a**, 485 mg, 34 %), and a trace amount of *N*,*N*,*N*′,*N*′-tetraethylurea (**8a**).

Reaction of Sodium Trichloroacetate with Elemental Selenium and Diethylamine under Ultrasonic Irradiation. A 10 ml HMPA suspended solution of a mixture of sodium trichloroacetate (927 mg, 5.00 mmol), NaH (400 mg (60% in oil), 10.0 mmol), elemental selenium (1.18 g, 15.0 mmol), and diethylamine (1.83 g, 25.0 mmol) was subjected to ultrasonic irradiation at room temperature for 2 h. The reaction mixture was quenched with an excess amount of water and the reaction mixture was subjected to the usual workup to give *N*,*N*,*N*′,*N*′-tetraethylselenourea (**7a**, 247 mg, 21%) and bis(*N*,*N*-diethylselenocarbamoyl) triselenide (**9a**, 225 mg, 16%).

Reaction of Chloroform with NaH, Elemental Selenium, and Diethylamine. A 5 ml HMPA solution of chloroform (358 mg, 3.00 mmol) was added to a 10 ml HMPA suspension of a mixture of NaH (360 mg (60% in oil), 9.00 mmol), elemental selenium (711 mg, 9.00 mmol), and diethylamine (1.10 g, 15.0 mmol), and the reaction mixture was stirred at 120—130 °C for 3 h under a N_2 atmosphere. The reaction mixture was quenched with an excess amount of water and the reaction mixture was subjected to the usual workup to give *N*,*N*,*N*′,*N*′-tetraethylselenourea (**7a**, 261 mg, 37%), *N*,*N*-diethylselenoformamide (**2a**, 64 mg, 13%), and a trace amount of bis(*N*,*N*-diethylselenocarbamoyl) triselenide (**9a**).

Reaction of Chloroform with NaH, Elemental Selenium, and Diethylamine under Ultrasonic Irradiation. A 10 ml HMPA suspension of a mixture of NaH (503 mg (60% in oil), 12.6 mmol), elemental selenium (992 mg, 12.6 mmol), chloroform (500 mg, 4.19 mmol), and diethylamine (1.53 g, 20.9 mmol) was subjected to ultrasonic irradiation at room temperature for 2 h. The reaction mixture was quenched with an excess amount of water and the reaction mixture was subjected to the usual workup to give *N*,*N*,*N*′,*N*′-tetraethylselenourea (**7a**, 292 mg, 30%) and bis(*N*,*N*-diethylselenocarbamoyl) triselenide (**9a**, 148 mg, 13%).

Treatment of Bis(*N*,*N*-diethylselenocarbamoyl) Triselenide (9a) with an Excess Amount of Diethylamine. A 10 ml HMPA solution of bis(*N*,*N*-diethylselenocarbamoyl) triselenide (**9a**, 563 mg, 1.00 mmol) and diethylamine (7.31 g, 10.0 mmol) was heated at 130 °C for 6 h under an Ar atmosphere. The reaction mixture was quenched with an excess amount of water. This reaction mixture was subjected to the usual workup to give *N*,*N*,*N*′,*N*′-tetraethylselenourea (**7a**, 405 mg, 86 %) and a trace amount of bis(*N*,*N*-diethylselenocarbamoyl) triselenide (**9a**).

Physical Data of 7. **7a (X=Se, $R^1=R^2=$Et):** Yellow oil; MS (*m*/*z*) 236 (M^+; bp, ^{80}Se); IR (neat) 2900, 1630, 1420, 1240, 1108 cm^{-1}; ^{1}H NMR ($CDCl_3$) $\delta=1.20$ (12H, t, $J=6.5$ Hz), 3.60 (8H, q, $J=6.5$ Hz). Found: C, 45.88; H, 8.87; N, 11.84%. Calcd for $C_9H_{20}N_2Se$: C, 45.95; H, 8.57; N, 11.91%.

7b (X=Se, $R^1=R^2=$Bu): Orange oil; MS (*m*/*z*) 348 (M^+; 54%, ^{80}Se); IR (neat) 2958, 2872, 1465, 1204, 1106, 741 cm^{-1}; ^{1}H NMR ($CDCl_3$) $\delta=0.80$—1.80 (28H, m), 3.84 (8H, t, $J=7.5$ Hz). Found: C, 57.33; H, 10.85; N, 8.10%. Calcd for $C_{16}H_{36}N_2Se$: C, 57.29; H, 10.82; N, 8.35%.

7c (X=Se, $R^1=R^2=-(CH_2)_5-$): Colorless plates, mp 78—79 °C (lit,[19] 79—80 °C).

Physical data of 9. **9a ($R^1=R^2=$Et):** Red needles, mp 135 °C (lit,[26,27] 136—137 °C).

9b ($R^1=R^2=$Bu): Red needles, mp 37—39 °C (lit,[27] 39—40 °C).

A Typical Procedure of mCPBA Oxidation of Selenoamides (2) or Selenoureas (9).[22,23] To a dichloromethane solution of a selenoamide (**2**, 1.00 mmol) or a selenourea (**7**, 1.00 mmol) was added a dichloromethane solution of mCPBA (259 mg (80%), 1.20 mmol). The reaction mixture was then stirred at 0 °C for 3 h. This reaction mixture was quenched with an aqueous Na_2SO_3 solution, and was extracted with dichloromethane. The organic layer was washed with an aqueous $NaHCO_3$ solution and with water, and was dried over anhydrous Na_2SO_4 powder. After the removal of the solvent, the residue was separated by column chromatography on silica gel using chloroform as an eluent to give the corresponding amides **4** or ureas **8** in quantitative yields.

Reaction of Benzyl Bromide with NaH, Elemental Selenium, and Diethylamine. A 5 ml HMPA solution of benzyl bromide (500 mg, 2.92 mmol) was added to a 10 ml volume of HMPA suspension of NaH (175 mg (60% in oil), 4.38 mmol), elemental selenium (462 mg, 5.85 mmol), and diethylamine (214 mg, 2.92 mmol). The reaction mixture was subjected to the ultrasonic irradiation at room temperature for 3 h under a N_2 atmosphere. This reaction mixture was quenched with an excess amount of water and the reaction mixture was subjected to the usual workup to give dibenzyl diselenide (**3b**, 69 mg, 14%), *N*,*N*-diethylselenobenzamide (**2b**, 9 mg, 1 %), and benzaldehyde (**4b**, 59 mg, 25%) along with a trace amount of unidentified products.

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