  Bull. Chem. Soc. Jpn., 61, 449—454 (1988)

Reaction of Benzeneseleninyl Chloride with Olefins in the Presence of a Lewis Acid. A Novel One Step Vinylic Chlorination

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(Received July 9, 1987)

In the presence of aluminum chloride benzeneseleninyl chloride was found to be an excellent vinylic chlorinating reagent of olefins under mild conditions. However, such olefins as styrene, *trans*-stilbene, and *trans*-1-phenylpropene afforded dichloro adducts under similar conditions. A plausible reaction mechanism involving positive chlorine intermediate is proposed.

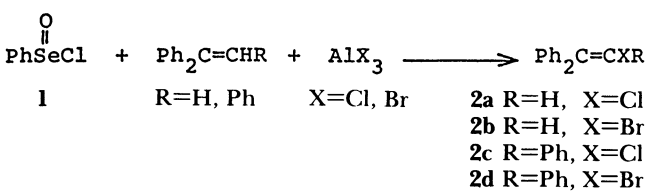
In recent years organic selenium reagents have become a very powerful tool in organic synthesis.[1] Of particular importance is the following discovery: a) Epoxides are converted into olefins by treatment with triphenylphosphine selenide in the presence of an acid,[2] b) selenoxides prepared by oxidation of selenides undergo clean syn elimination of selenenic acid to form olefins at or below room temperature,[3] c) epoxides are converted into allylic alcohols by ring opening with benzeneselenolate ion followed by selenoxide fragmentation and the intermediate β-hydroxy alkyl selenides are transformed into olefin,[4] d) selenium metal catalyze the reaction of amines and alcohols with carbon monoxide to give ureas and carbonates, respectively,[5] e) olefins are converted into ally alcohols by treatment with selenium dioxide,[6] and f) semicarbazones are transformed into 1,2,3-selenadiazoles by treatment with selenium dioxide which collapse at high temperatures to produce acetylenes.[7]

Benzeneseleninyl chloride (**1**) was first prepared by Ayrey et al. by the reaction of benzeneselenenyl chloride with ozone and is known to be highly hygroscopic and hydrolyzed to benzeneseleninic acid.[8] So far, little effort has been made to employ compound **1** as a synthetic tool; however, a few papers were found (reported by Czarny and Sosnovsky) in which aminodiphenylmethane and benzylamine were oxidized by **1** to give benzophenone and benzyl cyanide, respectively.[9,11] We found that a reaction of compound **1** with olefins in the presence of a Lewis acid gives chloro-substituted olefins at olefinic carbon. The results are described in this paper, and the mechanism is discussed.

Results and Discussion

The reaction of benzeneseleninyl chloride (**1**) with 1,1-diphenylethylene was carried out in dichloromethane in the presence of a Lewis acid at room temperature. When aluminum chloride was employed as a catalyst, the reaction occurred very smoothly and after stirring for 2 h at room temperature, 2-chloro-1,1-diphenylethylene (**2a**) was formed in 94% yield. However, such Lewis acids as iron(III) chloride and zinc chloride afforded the chlorinated compounds **2a** under similar conditions in 68 and 26% yield, respectively. The reaction proceeded very slowly when the reaction was carried out in the absence of a Lewis acid, and 2-chloro-1,1-diphenylethylene was obtained in 60% yield after 142 h at 40 °C.

When aluminum bromide was used as the catalyst instead of aluminum chloride in the reaction of **1** with 1,1-diphenylethylene, 2-bromo-1,1-diphenylethylene (**2b**) was obtained in 84% yield after stirring at room temperature for 1 h. The reaction of **1** with triphenylethylene in the presence of aluminum chloride and aluminum bromide under similar conditions afforded chlorotriphenylethylene (**2c**) and bromotriphenylethylene (**2d**) in quantitative yield, respectively. The results are summarized in Table 1.



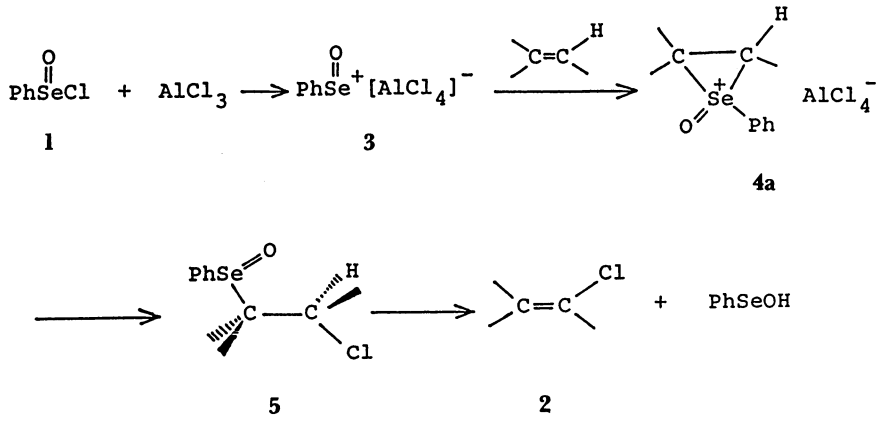
The present reaction seems to be an excellent halogenating method since a direct vinylic halogenation of olefins is hitherto unknown. A possible reaction mechanism shown in Scheme 1 accounts for these novel one-step vinylic chlorinations of olefins with **1**.

The aluminum catalyst abstracts chloride ion from benzeneseleninyl chloride to give benzeneseleninyl cation species **3** and aluminum tetrachloride anion species, as is known for the acylium ion intermediate in the Friedel-Crafts acylation of acyl chloride with aluminum chloride. The electrophilic addition of **3** to olefin affords cyclic selenoxonium ion intermediate **4a**, which is attacked by a chloride ion to give a ring-

Table 1. Reaction of Benzeneseleninyl Chloride with Vinyl-Substituted Arenes at Room Temperature

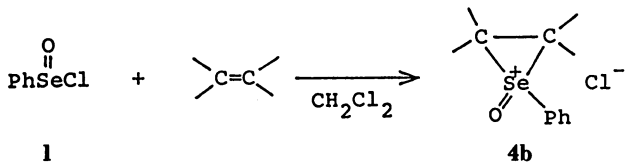
R in Ph_2C=CHR	Catalyst	Reaction time/h	Product	Yield/%
H	None	140[a]	**2a**	60
H	$AlCl_3$	2	**2a**	94
H	$FeCl_3$	2	**2a**	68
H	$ZnCl_2$	2	**2a**	26
H	$AlBr_3$	1	**2b**	84
Ph	$AlCl_3$	3	**2c**	100
Ph	$AlBr_3$	3	**2d**	97

a) The reaction was carried out at 40 °C.

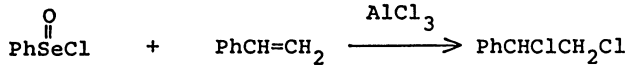


Scheme 1.

opening adduct **5**. The following syn-elimination of benzeneselenenic acid from **5** gives the final vinylic chlorination product **2**. The syn-elimination of benzeneseleninyl group with β-hydrogen is well-known and this method has been given much attention for the synthesis of olefins.[3] The reason why the reaction of **1** with 1,1-diphenylethylene in the absence of aluminum chloride is slow can be best accounted for by the fact that direct electrophilic reaction of **1** to the olefin forming cyclic selenoxonium intermediate **4b** is slow: meanwhile, the benzeneseleninyl cation species **3** reacts with olefin very smoothly.



The reaction of **1** with phenyl-substituted ethylenes such as styrene, *trans*-stilbene, and *trans*-1-phenylpropene was carried out in the presence of aluminum chloride. In the reaction of **1** with styrene, styrene dichloride was isolated in 48% yield, and no formation of chloro-substituted styrene obtainable from substitution at olefinic hydrogen was observed.



In the reaction of **1** with stilbene, *dl*- and *meso*-1,2-dichloro-1,2-diphenylethane **6a**, **6b** were isolated in 21 and 31% yield, respectively.

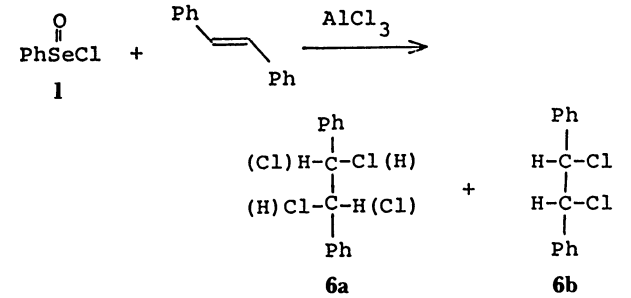
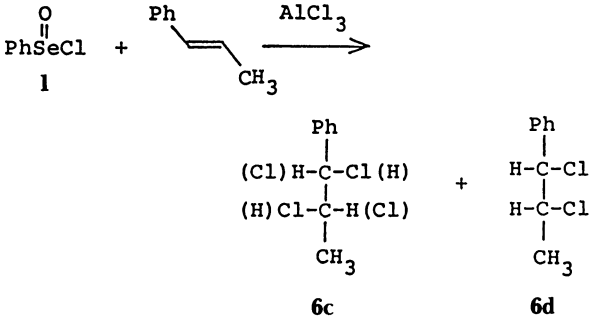


Table 2. α-Chlorination of α,β-Unsaturated Carbonyl Compounds **7** with Benzeneseleninyl Chloride Catalyzed by $AlCl_3$ at 40 °C

	Compound **7**			Reaction time/h	Product	Yield/%
	R_1	R_2	R_3			
7a	Me	H	H	2	**8a**	77
7b	Ph	H	H	55	**8b**	61
7c	Ph	Ph	H	71	**8c**	45
7d	Ph	H	Me	18	**8d**	50
7e	Ph	H	Ph	78	**8e**	30
7f	H	H	OEt	26	**8f**	70
7g	H	H	OBu^n	22	**8g**	46
7h	Me	H	OMe	23	**8h**	96
7i	Me	H	OEt	23	**8i**	88
7j	Ph	H	OMe	30	**8j**[a]	11
7k	Ph	H	OEt	26	**8k**[b]	17

a) The mixture of *threo*- and *erythro*-methy 2,3-dichloro-3-phenyl propionate was isolated in 33% yield together with **8j**. b) The mixture of *threo*- and *erythro*-ethyl 2,3-dichloro-3-phenyl propionate was isolated in 48% yield together with **8k**.

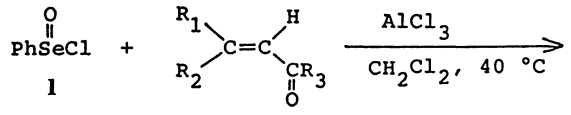
Similarly, in the reaction of *trans*-1-phenylpropene, *threo*- and *erythro*-1,2-dichloro-1-phenylpropane **6c**, **d** were obtained in 38 and 23% yield, respectively.



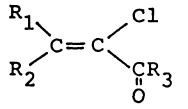
Against our expectations, the reaction of **1** with these phenyl-substituted ethylenes did not afford chloro-substituted arenes but formed dichloro adducts. It is difficult to explain these addition products by a reaction mechanism involving the cyclic selenoxonium ion intermediate shown in Scheme 1.

The reaction of **1** with α,β-unsaturated carbonyl

compounds in the presence of aluminum chloride was carried out at 40 °C. The chloro-substituted products at α-hydrogen were obtained in moderate to high yield. The structure of the products was determined by IR, ^{1}H NMR, ^{13}C NMR, and mass spectra (see experimental section). The results are summarized in Table 2.



1 + **7** → ($AlCl_3$, CH_2Cl_2, 40 °C)



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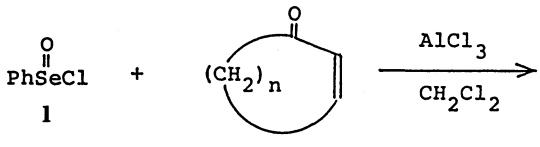
In the case of the reaction of **1** with methyl and ethyl cinnamate, dichloro adducts *threo*- and *erythro*-2,3-dichloro-3-phenylpropionic acid methyl ester (33%) and *threo*- and *erythro*-2,3-dichloro-3-phenylpropionic acid ethyl ester (48%) were formed together with chloro-substituted products **8j** and **8k**, respectively. The results mean that the addition and substitution occurr competitively.

The reaction of **1** with 2-cyclopenten-1-one (**9a**) in the presence of aluminum chloride at room temperature afforded 2-chloro-2-cyclopenten-1-one (**10a**) in 47% yield. Similarly, 2-cyclohexen-1-one (**9b**) and 2-cyclohepten-1-one (**9c**) were chlorinated by **1** in the presence of aluminum chloride to give corresponding 2-chlorocycloalkenones **10b** and **10c** in moderate to good yield. 1,4-Benzoquinone was also chlorinated by **1** under similar conditions to give 2-chloro-1,4-benzoquinone (**10d**) in 44% yield. However, no chloro-substituted product was obtained in the reaction of **1** with 1,4-naphthoquinone catalyzed by aluminum chloride under various reaction conditions. The results are summarized in Table 3.



1 + **9a** n=2, **9b** n=3, **9c** n=4 → ($AlCl_3$, CH_2Cl_2)

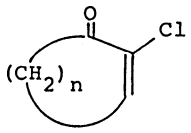


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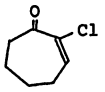
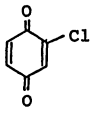
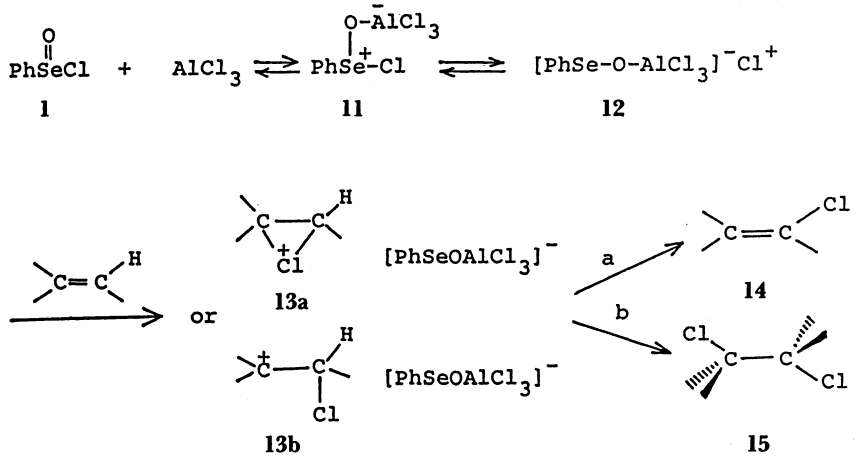
Table 3. α-Chlorination of Cyclic α,β-Unsaturated Ketones

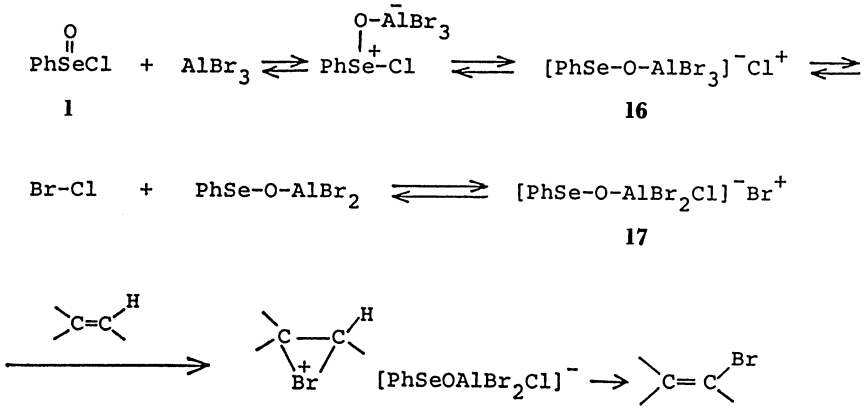
Ketone	Reaction temp/°C	Reaction time/h	Product	Yield/%
9a	Room temp	48	 **10a**	47
9b	0	9	 **10b**	41
9c	0	7	 **10c**	56
1,4-Benzoquinone	40	22	 **10d**	44

The results in the Tables 1, 2, and 3 show that the reaction of benzeneseleninyl chloride (**1**) with olefins catalyzed by aluminum chloride provides chloro-substituted compounds at vinyl position in one step in good yield; therefore, **1** can be regarded as an excellent vinylic chlorinating reagent and a new synthetic tool for chlorination.

The reaction mechanism shown in Scheme 1 can explain the vinylic chlorination products but can not



Scheme 2.



Scheme 3.

easily explain the dichloro-addition products observed in the reaction of **1** with such olefins as styrene, *trans*-1-phenylpropene, and *trans*-stilbene. An alternative mechanism shown in Scheme 2 interprets both the chloro-substituted products at the vinyl position and the dichloro-adducts from the common reactive intermediate.

Aluminum chloride does not abstract the chloride ion but reacts with the oxygen atom of the benzeneseleninyl chloride to form the intermediate **11** which easily converts to chloronium trichloro(phenylselenooxy)aluminate (**12**). The following electrophilic reaction of the chloronium ion with olefin gives either a chloronium ion **13a** or a carbocation intermediate **13b**. If the chloride ion of the trichloro(phenylselenooxy)aluminate species attacks the hydrogen atom of intermediate **13** (path a), chloro-substituted vinyl products **14** are obtained. On the other hand, when a chloride ion of the trichloro(phenylselenooxy)aluminate species attacks the carbon atom of intermediate **13a** or the carbocation intermediate **13b** (path b), dichloro adducts are obtained. The reaction of path a will occur in the following cases: a) the substituents of the olefin are a bulky group, b) the β-hydrogen of the cation intermediate **13a** or **13b** is relatively acidic. Case a) was observed in such olefins as 1,1-diphenylethylene and triphenylethylene, and case b) was observed in α,β-unsaturated carbonyl compounds. Such olefins as styrene, *trans*-1-phenylpropene, and *trans*-stilbene formed dichloro adducts since these olefins do not conform to these two cases.

When aluminum bromide was employed instead of aluminum chloride in the reaction of **1** with 1,1-diphenylethylene, 2-bromo-1,1-diphenylethylene was obtained in 84% yield, and no formation of 2-chloro-1,1-diphenylethylene was observed. This means that chloronium tribromo(phenylselenooxy)aluminate (**16**), formed by the reaction of **1** with aluminum bromide, transforms rapidly to bromonium dibromochloro-(phenylselenooxy)aluminate(**17**). The following electrophilic reaction of the bromonium ion with olefin gives the bromo-substituted products as shown in Scheme 3.

To justify the mechanism shown in Scheme 2, ^{77}Se NMR studies were carried out. The ^{77}Se NMR signal of benzeneseleninyl chloride in dichloromethane appeared at 850 ppm, shifted to 670 ppm when equimolar ammounts of aluminum chloride were added to a solution of **1** in dichloromethane (diphenyl diselenide was employed as the internal standard). The results suggest that the $PhSe^{+}[AlCl_4]^{-}$ species (**3**) is not formed by the addition of aluminum chloride to **1** (as shown in Scheme 1), since one can expect a down-field shift more than 850 ppm about such a benzeneseleninyl cation species **3** from diphenyl diselenide. Thus, we believe that the observation of the 180 ppm up-field shift can be attributed to the formation of chloronium trichloro(phenylselenooxy)aluminate intermediate (**12**).

Experimental

Measurement. Melting points and boiling points were uncorrected. The infrared absorption spectra were determined on a Hitachi Model 260-10 spectrometer with samples as either neat liquid or KBr disks. The proton magnetic resonance spectra were recorded at 60 MHz by using a JEOL JNM-PMX 60 SI spectrometer with Me_4Si as an internal standard in $CDCl_3$. The ^{13}C and ^{77}Se NMR spectra were recorded by using a JEOL JNM-FX 90Q spectrometer with Me_4Si and PhSeSePh as an internal standard, respectively. Gas chromatography was performed by using a Hitachi 163 and 263-30 gas chromatograph using SE 30 (10%), 1 m column. The gel-permeation chromatography was performed by using a JAI Model LC-08 liquid chromatograph with a JAIGEL-1H column (20×600 mm×2) using chloroform as an eluent. Mass spectra were determined with a JEOL JMX-DX 300 mass spectrometer with a JEOL JMA 5000 Mass Data System at an ionizing voltage of 20—70 eV.

Materials. Benzeneselenenyl chloride of Nakarai Chemicals was distilled prior to use; bp 82 °C/3 mmHg† (120 °C/20 mmHg).[10] Benzeneseleninyl chloride (**1**) was prepared by ozonization of benzeneselenenyl chloride with stirring in dry dichloromethane at −70 °C until the orange-red color faded

† 1 mmHg=133.322 Pa.

to a light yellow[8,11] by introducing ozone prepared by a Nippon Ozone Model 0-3-2 ozonizer. The prepared benzeneseleninyl chloride was used in reactions with olefins in situ since the compound is extremely hygroscopic and care must be taken to avoid moisture.

General Procedure for the Reaction of Benzeneseleninyl Chloride with Olefins. To a stirred solution containing 2.0 mmol of benzeneseleninyl chloride (**1**) in 20 cm^3 of dichloromethane under nitrogen bubbling in an ice bath was added 2 mmol of an olefin and 2 mmol of a Lewis acid. The mixture was stirred for an adequate time (until **1** has almost consumed by TLC analysis) at 0 °C or room temperature. Water (30 cm^3) was added to the reaction mixture, and the organic layer was separated and dried over anhydrous magnesium sulfate. The reaction products were isolated by gel-permeation chromatograph, and the structure was identified on the basis of their spectroscopic data.

2-Chloro-1,1-diphenylethylene (2a): Bp 118 °C/0.5 mmHg (298 °C);[12] IR (neat) 3070, 1600, 1500, 1445, 830, 755, and 695 cm^{-1}; ^1H NMR ($CDCl_3$) δ=6.57 (1H, s), 7.21 (5H, s), and 7.33 (5H, s); MS m/z 214 (^{35}Cl, M^+).

2-Bromo-1,1-diphenylethylene (2b): Bp 125—126 °C/1 mmHg (175—176 °C/11.5 mmHg);[13] IR (neat) 3065, 1590, 1500, 1445, 1220, 1075, 765, 740, and 695 cm^{-1}; ^1H NMR ($CDCl_3$) δ=6.70 (1H, s), 7.18 (5H, s), and 7.30 (5H, s); MS, m/z 258 (^{79}Br, M^+).

Chlorotriphenylethylene (2c): Mp 116—117 °C (117 °C);[14] IR (KBr) 3060, 1600, 1495, 1445, 750, and 695 cm^{-1}; ^1H NMR ($CDCl_3$) δ=6.81—7.47 (15H, m); MS m/z 290 (^{35}Cl, M^+).

1,2-Dichloro-1-phenylethane:[15] IR (neat) 3000, 1485, 1445, 1195, 1075, 940, 920, and 695 cm^{-1}; ^1H NMR ($CDCl_3$) δ=3.89 (2H, d, J=7.6 Hz), 4.95 (1H, t, J=7.6 Hz), and 7.29 (5H, s); MS m/z 174 (^{35}Cl, M^+).

***dl*-1,2-Dichloro-1,2-diphenylethane (6a):** Mp 93 °C (93 °C);[16] IR (KBr) 3070, 1490, 1450, 1230, 1205, 1070, 775, 745, and 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ=5.18 (2H, s) and 7.09—7.28 (10H, m); MS m/z 250 (^{35}Cl, M^+).

***meso*-1,2-Dichloro-1,2-diphenylethane (6b):** Mp 190 °C (191 °C);[16] IR (KBr) 3010, 1490, 1440, 1225, 1175, 1065, 805, 760, and 685 cm^{-1}; ^1H NMR ($CDCl_3$) δ=5.17 (2H, s) and 7.36 (10H, s); MS m/z 250 (M^+).

2-Chloro-2-butenal (8a): Bp 147—148 °C (147—150 °C);[17] IR (neat) 1695 and 1175 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.06 (3H, d, J=6.6 Hz), 6.93 (1H, q, J=6.6 Hz), and 9.27 (1H, s); MS m/z 104 (^{35}Cl, M^+).

2-Chloro-3-phenylpropenal (8b): Bp 90—91 °C/1 mmHg (132—134 °C/8 mmHg);[17] IR (neat) 1685 and 1295 cm^{-1}; ^1H NMR ($CDCl_3$) δ=7.36—8.09 (6H, m) and 9.41 (1H, s); MS m/z 166 (^{35}Cl, M^+).

2-Chloro-3,3-diphenylpropenal (8c): Mp 117—119 °C; IR (KBr) 1685 and 1150 cm^{-1}. ^1H NMR ($CDCl_3$) δ=7.01—7.30 (10H, m) and 9.34 (1H, s); MS m/z 242 (^{35}Cl, M^+); Found: m/z 242.0492. Calcd for $C_{15}H_{11}OCl$: M, 242.0498.

3-Chloro-4-phenyl-3-buten-2-one (8d): IR (neat) 1695 and 1210 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.52 (3H, s) and 7.23—7.92 (6H, m); MS m/z 180 (^{35}Cl, M^+); Found: m/z 180.0346. Calcd for $C_{10}H_9OCl$: M, 180.0342.

2-Chloro-1,3-diphenyl-2-propen-1-one (8e): IR (neat) 1660 and 1250 cm^{-1}; ^1H NMR ($CDCl_3$) δ=7.27—7.91 (11H, m); ^{13}C NMR ($CDCl_3$) δ=128.39, 128.56, 129.48, 129.86, 130.34, 130.56, 132.46, 132.94, 136.84, 139.34, and 191.07; MS m/z 242 (^{35}Cl, M^+); Found: m/z 242.0497. Calcd for $C_{15}H_{11}OCl$: M, 242.0498.

Ethyl 2-Chloropropenoate (8f): IR (neat) 1745 and 1275 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.33 (3H, t, J=7.2 Hz), 4.28 (2H, q, J=7.2 Hz), 5.92 (1H, d, J=2.0 Hz), and 6.45 (1H, t, J=2.0 Hz); MS m/z 134 (^{35}Cl, M^+); Found: m/z 134.0139. Calcd for $C_5H_7O_2Cl$: M, 134.0134.

Butyl 2-Chloropropenoate (8g): IR (neat) 1745 and 1280 cm^{-1}. ^1H NMR ($CDCl_3$) δ=0.80—2.00 (7H, m), 4.20 (2H, t, J=7.2 Hz), 5.94 (1H, d, J=2.0 Hz), and 6.44 (1H, d, J=2.0 Hz); MS m/z 162 (^{35}Cl, M^+); Found: m/z 162.0452. Calcd for $C_7H_{11}O_2Cl$: M, 162.0447.

Methyl 2-Chloro-2-butenoate (8h): Bp 160—161 °C (161 °C);[18] IR (neat) 1745 and 1275 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.94 (3H, d, J=7.0 Hz), 3.78 (3H, s), and 7.10 (1H, q, J=7.0 Hz); MS m/z 134 (^{35}Cl, M^+).

Ethyl 2-Chloro-2-butenoate (8i): Bp 175—176 °C (176 °C);[18] IR (neat) 1725 and 1265 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.33 (3H, t, J=7.2 Hz), 1.94 (3H, d, J=7.2 Hz), 4.24 (2H, q, J=7.8 Hz), and 7.07 (1H, q, J=7.2 Hz); ^{13}C NMR ($CDCl_3$) δ=14.09, 14.91, 61.98, 125.96, 137.07, and 162.36; MS m/z 148 (^{35}Cl, M^+).

Methyl 2-Chloro-3-phenylpropenoate (8j): Mp 32—33 °C (33.0—33.5 °C);[19] IR (neat) 1730 and 1270 cm^{-1}; ^1H NMR ($CDCl_3$) δ=3.90 (3H, s) and 7.19—7.62 (6H, m); ^{13}C NMR ($CDCl_3$) δ=53.37, 121.84, 128.56, 130.24, 130.67, 132.95, 137.23, and 163.94; MS m/z 196 (^{35}Cl, M^+).

Ethyl 2-Chloro-3-phenylpropenoate (8k): Bp 104—105 °C/1 mmHg (209 °C/75 mmHg);[20] IR (neat) 1735 and 1265 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.36 (3H, t, J=7.4 Hz), 4.32 (2H, q, J=7.4 Hz), and 7.17—8.16 (6H, m); ^{13}C NMR ($CDCl_3$) δ=14.26, 62.58, 122.28, 128.51, 130.13, 130.62, 133.00, 136.90, and 163.39; MS m/z 210 (^{35}Cl, M^+).

Methyl *threo*-2,3-Dichloro-3-phenylpropionate:[21] ^1H NMR ($CDCl_3$) δ=3.57 (3H, s), 4.61 (1H, d, J=8.4 Hz), 5.42 (1H, d, J=8.4 Hz), and 7.33 (5H, s); MS m/z 232 (^{35}Cl, M^+).

Methyl *erythro*-2,3-Dichloro-3-phenylpropionate:[21] IR (KBr) 1750 and 1210 cm^{-1}; ^1H NMR ($CDCl_3$) δ=3.84 (3H, s), 4.54 (1H, d, J=10.8 Hz), 5.13 (1H, d, J=10.8 Hz), and 7.33 (5H, s); MS m/z 232 (^{35}Cl, M^+).

Ethyl *threo*-2,3-Dichloro-3-phenylpropionate:[21] ^1H NMR ($CDCl_3$) δ=1.06 (3H, t, J=7.4 Hz), 4.02 (2H, q, J=7.4 Hz), 4.63 (1H, d, J=8.6 Hz), 5.27 (1H, d, J=8.6 Hz), and 7.35 (5H, s); MS, m/z 246 (^{35}Cl, M^+).

Ethyl *erythro*-2,3-Dichloro-3-phenylpropionate:[21] IR (neat) 1750 and 1275 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.32 (3H, t, J=7.4 Hz), 4.28 (2H, q, J=7.4 Hz), 4.56 (1H, d, J=10.4 Hz), 5.17 (1H, d, J=10.4 Hz), and 7.31 (5H, s); MS m/z 246 (^{35}Cl, M^+).

2-Chloro-2-cyclopenten-1-one (10a): IR (neat) 1730 and 1300 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.35—2.86 (4H, m) and 7.51 (1H, t, J=2.8 Hz); MS, m/z 116 (^{35}Cl, M^+); Found: m/z 116.0032. Calcd for C_5H_5OCl: M, 116.0029.

2-Chloro-2-cyclohexen-2-one (10b): Mp 70—72 °C (70 °C);[22] IR (KBr) 1680 and 1320 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.78—2.75 (6H, m) and 7.07 (1H, t, J=4.8 Hz); MS, m/z 130 (^{35}Cl, M^+); Found: m/z 130.0192. Calcd for C_6H_7OCl: M, 130.0185.

2-Chloro-2-cyclohepten-1-one (10c): IR (neat) 1690 and 1350 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.34—2.91 (8H, m) and 6.95 (1H, t, J=6.8 Hz); MS m/z 144 (^{35}Cl, M^+); Found: m/z 144.0338. Calcd for C_7H_9OCl: M, 144.0342.

2-Chloro-1,4-benzoquinone (10d): Mp 55—56 °C (57 °C);[23] IR (KBr) 1655 and 1285 cm^{-1}; ^1H NMR ($CDCl_3$) δ=6.79 (2H, s) and 6.95 (1H, s); MS m/z 142 (^{35}Cl, M^+).

^{77}Se NMR Studies. A solution containing 1.92 g (10 mmol) of benzeneselenenyl chloride in 20 cm^3 of dry dichloromethane was ozonized at −50 °C. A part of the solution containing benzeneseleninyl chloride (**1**) was transferred to a NMR tube, and the ^{77}Se NMR spectrum was determined. The ^{77}Se NMR signal was observed at 850 ppm from diphenyl diselenide as the internal standard. Then, to a solution of benzeneseleninyl chloride prepared by the same manner described above was added 1.33 g (10 mmol) of aluminum chloride, and the mixture was stirred for 10 min at −50 °C. A part of the solution was transferred to a NMR tube, and the ^{77}Se NMR was determined. The ^{77}Se NMR signal was observed at 670 ppm from diphenyl diselenide as the internal standard.

References

1) For excellent reviews on organoselenium chemistry, see "Organic Selenium Compounds: Their Chemistry and Biology," ed by D. L. Klaymen and W. H. H. Grünther, John Wiley & Sons, New York (1973); "The Chemistry of Organic Selenium and Tellurium Compounds," ed by S. Patai and Z. Rappoport, John Wiley & Sons, New York (1986), Vol. 1; C. Paulmier, "Selenium Reagents and Intermediates in Organic Synthesis," ed by J. E. Baldwin, Pergamon Press, Oxford (1986); D. J. Clive, *Tetrahedron*, **34**, 1049 (1978); H. J. Reich, *Acc. Chem. Res.*, **12**, 22 (1979); K. C. Nicolaou, *Tetrahedron*, **37**, 4097 (1981); J. V. Comasseto, *J. Organomet. Chem.*, **253**, 131 (1983); D. Liotta, *Acc. Chem. Res.*, **17**, 28 (1984).

2) D. L. J. Clive and C. V. Denyer, *J. Chem. Soc., Chem. Commun.*, **1973**, 253.

3) D. L. J. Clive, *J. Chem. Soc., Chem. Commun.*, **1973**, 695; K. B. Sharpless, M. W. Young, and R. F. Lauer, *Tetrahedron Lett.*, **1973**, 1979; H. J. Reich, I. L. Reich, and J. M. Renga, *J. Am. Chem. Soc.*, **95**, 5813 (1973); H. J. Reich, J. M. Reng, and I. L. Reich, *ibid.*, **97**, 5434 (1975).

4) K. B. Sharpless, K. M. Gordon, R. F. Lauer, D. W. Patrick, S. P. Singer, and M. W. Young, *Chemica Scripta*, **8A**, 9 (1975); K. B. Sharpless and R. F. Lauer, *J. Am. Chem. Soc.*, **95**, 2697 (1973); P. A. Grieco, J. A. Noguez, and Y. Masaki, *Tetrahedron Lett.*, **1975**, 4213; W. Dumont, P. Bayet, and A. Krief, *Angew. Chem., Int. Ed. Engl.*, **13**, 806 (1974).

5) N. Sonoda, T. Yasuhara, K. Kondo, T. Ikehara, and S. Tsutsumi, *J. Am. Chem. Soc.*, **93**, 6344 (1971); K. Kondo, N. Sonoda, and H. Sakurai, *Chem. Lett.*, **1974**, 1429; K. Kondo, N. Sonoda, K. Yoshida, M. Koishi, and S. Tsutsumi, *Chem. Lett.*, **1972**, 401; K. Kondo, N. Sonoda, and S. Tsutsumi, *Tetrahedron Lett.*, **1971**, 4885; K. Kondo, N. Sonoda, and H. Sakurai, *Bull. Chem. Soc. Jpn.*, **48**, 108 (1975).

6) K. B. Sharpless and R. F. Lauer, *J. Am. Chem. Soc.*, **94**, 7154 (1972); D. Arigoni, A. Vasella, K. B. Sharpless, and H. P. Jensen, *ibid.*, **95**, 7917 (1973); H. P. Jensen and K. B. Sharpless, *J. Org. Chem.*, **40**, 264 (1975).

7) I. Lalezari, A. Shafiee, and M. Yalpani, *Tetrahedron Lett.*, **1969**, 5105; I. Lalezari, A. Shafiee, and M. Yalpani, *Angew. Chem., Int. Ed. Engl.*, **9**, 464 (1970); H. Meier and H. Gugel, *Synthesis*, **1976**, 338.

8) G. Ayrey, D. Barnard, and D. T. Woodbridge, *J. Chem. Soc.*, **1962**, 2089.

9) M. R. Czarny, *Synth. Commun.*, **6**, 285 (1976); G. Sosnovsky, J. A. Krogh, *Z. Naturforsch., B, Anorg. Chem., Org. Chem.*, **34B**, 511 (1979).

10) O. Behaghel and H. Seibert, *Ber.*, **66**, 708 (1933).

11) H. J. Reich, J. M. Renga, and I. L. Reich, *J. Am. Chem. Soc.*, **97**, 5434 (1975).

12) W. P. Bettenberg, *Justus Liebigs Ann. Chem.*, **279**, 324 (1894).

13) P. Lipp, *Ber.*, **56**, 567 (1923); G. Wittig and R. Kethur, *ibid.*, **69**, 2078 (1936).

14) E. Bergmann and A. Bondi, *Ber.*, **64**, 1455 (1931).

15) H. Bilz, *Justus Liebigs Ann. Chem.*, **296**, 263 (1897); G. H. Coleman and A. W. Campbell, *J. Am. Chem. Soc.*, **50**, 2754 (1928).

16) Th. Zincke, *Ber.*, **10**, 996 (1877); **12**, 115 (1879); P. Pfeiffer, *Ber.*, **45**, 1810 (1912); P. Pfeiffer and B. Eistert, *J. Pract. Chem.*, **124**, 168 (1930).

17) H. Hibbert, E. O. Houghton, and K. A. Taylor, *J. Am. Chem. Soc.*, **51**, 611 (1929).

18) F. D. Chattaway and H. Irving, *J. Chem. Soc.*, **1929**, 1038.

19) R. Stoermer and H. Kirchner, *Ber.*, **53**, 1289 (1920).

20) K. V. Auwers and E. Schmellenkamp, *Ber.*, **54**, 624 (1921).

21) C. Liebermann and H. Finkenbeiner, *Ber.*, **26**, 833 (1893); **28**, 2235 (1895).

22) A. Kotz and K. Richter, *J. Pract. Chem.*, **111**, 373 (1925).

23) E. Wöhler, *Justus Liebigs Ann. Chem.*, **51**, 145 (1844); G. Städeler, *ibid.*, **69**, 300 (1849).