Generation and Thermal Reactions of 2-Methyl-4-oxo-2-selenoniochroman-3-ide

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The thermal reaction of 2-methyl-4-oxo-2-selenoniochroman-3-ide (**4**) in aprotic solvents afforded (*E*)-bis-[2-[(methylseleno)methyl]benzoyl]ethylene (**5**) and *trans*-1,2,3-tris[2-[(methylseleno)methyl]benzoyl]cyclopropane (**6**) via a carbene intermediate. Ethanol reacted thermally with **4** to open the chroman ring, giving ethyl 2-[(methylseleno)methyl]benzoate (**9a**) and ethyl 2-(ethoxymethyl)benzoate (**10a**), whereas reaction with methanol yielded only methyl 2-[(methylseleno)methyl]benzoate (**9b**). Hydrolysis of ylide **4** eliminated dimethyl selenide, giving phthalide and 2-(hydroxymethyl)benzoic acid.

Introduction

Reactions of selenonium ylides are generally similar to those of sulfonium ylides.[1] However, since the Se–C bond is longer and weaker than the S–C bond, and the bond angle C–Se–C is smaller than C–S–C, cyclic selenium compounds should be more strained than their sulfur analogues. Accordingly, we should expect some differences in the reactivities of cyclic selenonium ylides and cyclic sulfonium ylides. Mislow and his co-workers have reported on the chemistry of some selenabenzenes and have shown that selenabenzenes are less stable than thiabenzenes.[2]

We report here on the generation and thermal reactions of 2-methyl-4-oxo-2-selenoniochroman-3-ide (**4**), a cyclic selenonium ylide stabilized by an electron-withdrawing group.

Results and Discussion

2-Selenochroman-4-one (**2**) was obtained in excellent yield from 2-(carboxybenzyl)selenoacetic acid (**1**) by Renson's method:[3] ring closure with potassium acetate in acetic anhydride followed by hydrolysis with dilute hydrochloric acid. Methylation of **2** with methyl iodide and silver tetrafluoroborate gave 2-methyl-4-oxo-2-selenochromanium tetrafluoroborate (**3**) in quantitative yield. The structure of **3** was established by its ^{1}H NMR spectrum, which showed a singlet at δ 2.80 assigned to the Se-methyl group and its IR spectrum, which had the absorption bands at 1640 and 1060 cm^{-1} assigned to C=O and BF_4^-, respectively.

Deprotonation of **3** with triethylamine was very slow, but could be accomplished with sodium hydride or a sodium alkoxide. However, ylide **4** thus produced gradually decomposed at room temperature and was not isolated.

Ylide **4** generated in situ from **3** and an equimolar amount of sodium hydride was refluxed for 12 h under a nitrogen atmosphere in aprotic solvents. The principal product was *trans*-1,2,3-tris[2-[(methylseleno)methyl]-cyclopropane (**6**, 20–28%), with lesser amounts of (*E*)-bis[(2-[(methylseleno)methyl]ethylene (**5**) and 2-selenochroman-4-one (**2**) (Scheme I and Table I).

This reaction is assumed to proceed via a carbene intermediate as shown in Scheme I. We attempted to trap the carbene with cyclohexene, but a norcarane derivative was not obtained. However, it is known that a norcarane is produced from cyclohexene in only a low yield when a more reactive nucleophile is present in the reaction of sulfur ylides containing a phenacyl group,[4] and **4** is apparently a much more effective nucleophile than cyclohexene.

Scheme I

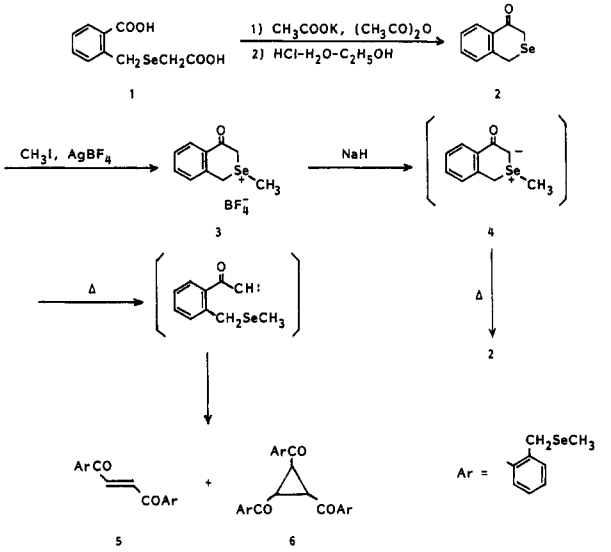


Table I. Thermal Reaction of 2-Methyl-4-oxo-2-selenoniochroman-3-ide (4) in Aprotic Solvents

solvent	yield (%) 2	5	6
benzene	13	14	28
tetrahydrofuran	11	2	20
dichloromethane	4	11	23
acetonitrile	3	trace[a]	23

[a] Trace < 2%.

The ^{1}H NMR spectrum of **5** showed three singlets at δ 1.94, 4.08, and 7.53 assigned to the Se-methyl, benzyl, and olefin protons, respectively, and the fragmentation pattern of its mass spectrum showed the presence of two Se-methyl groups. Its IR spectrum exhibited an absorption band of the carbonyl groups at 1640 cm^{-1}. Comparison of these ^{1}H NMR and IR spectra with those of (*E*)- and (*Z*)-dibenzoylethylenes led us to assign the *E* configuration to **5**;[5,6] the *Z* isomer was not obtained.

The ^{1}H NMR spectrum of **6** showed three singlets at δ 1.88, 1.91, and 1.95 assigned to the three Se-methyl groups.

(1) (a) Reich, H. J. *Acc. Chem. Res.* **1979**, *12*, 22–30. (b) Dumont, W.; Bayet, P.; Krief, A. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 274–275. (c) Gassman, P. G.; Miura, T.; Mossman, A. *J. Org. Chem.* **1982**, *47*, 954–959.

(2) Stackhouse, J.; Senkler, G. H., Jr.; Maryanoff, B. E.; Mislow, K. *J. Am. Chem. Soc.* **1974**, *96*, 7835–7836.

(3) Renson, M.; Pirson, P. *Bull. Soc. Chim. Belg.* **1966**, *75*, 456–464.

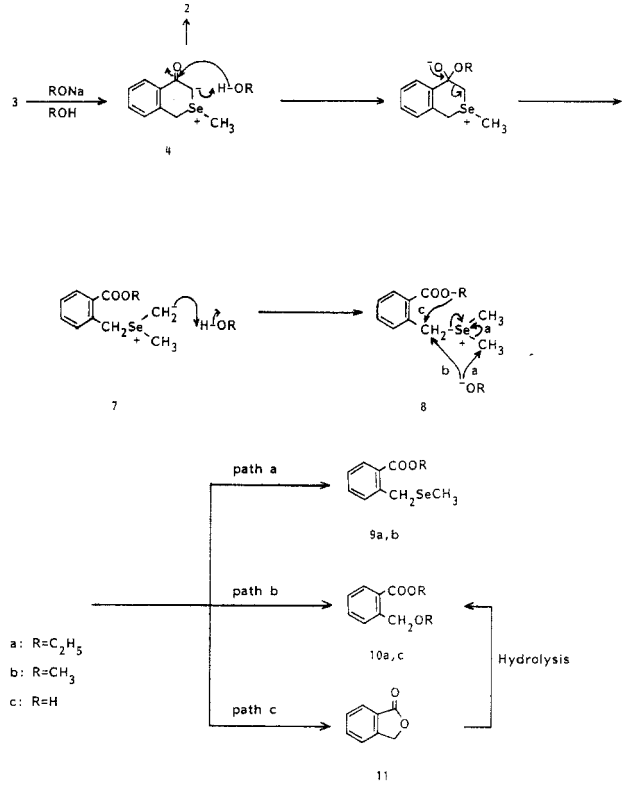
(4) Trost, B. M. *J. Am. Chem. Soc.* **1967**, *89*, 138–142.

(5) (*E*)-Dibenzoylethylene: IR (KBr) 1655 (ref 6a) or 1640 cm^{-1} (ref 6b); ^{1}H NMR ($CDCl_3$) δ 7.97 (olefin-H) (ref 6c). *Z* isomer: IR (KBr) 1665 cm^{-1} (ref 6a); ^{1}H NMR ($CDCl_3$) δ 7.11 (ref 6a) or 7.16 (olefin-H) (ref 6c).

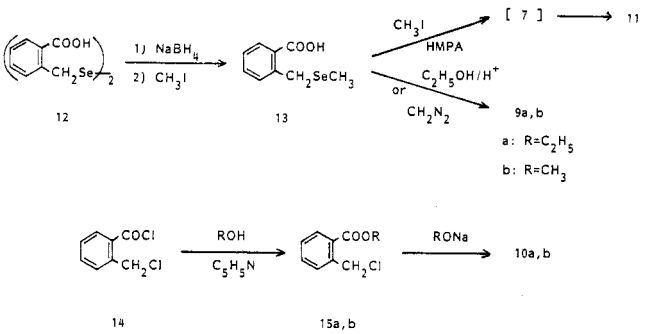
(6) (a) Takebayashi, M.; Ibata, T.; Ueda, K. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 1500–1505. (b) Sugiyama, N.; Kashima, C. *Ibid.* **1970**, *43*, 1875–1877. (c) Kreutzberger, A.; Kalter, P. A. *J. Org. Chem.* **1960**, *25*, 554–556.

0022-3263/87/1952-1397$01.50/0

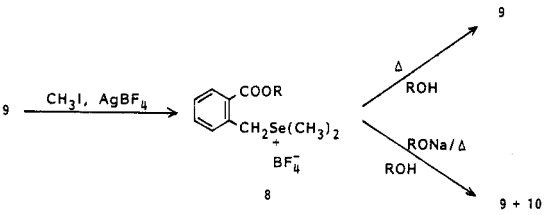
Scheme II



Scheme III



Scheme IV



The ^{13}C NMR spectrum showed absorptions of Se-methyl carbons at δ 4.7, 4.9, and 5.0, benzyl carbons at δ 25.6, 26.2, and 26.4, and cyclopropane carbons at δ 34.7 and 39.5. Comparison of these peaks with those of *trans*-1,2,3-tribenzoylcyclopropane[7] led us to assign the trans structure to **6**.

Ylide **4** generated in situ from **3** with an equimolar amount of sodium ethoxide was refluxed for 6 h under a nitrogen atmosphere to investigate the thermal reaction of **4** in ethanol. The ring-opened products ethyl 2-[(methylseleno)methyl]benzoate (**9a**) and ethyl 2-(ethoxymethyl)benzoate (**10a**) were obtained in 16% yield each (Scheme II). Other products were too complex to be isolated.

The ^1H NMR spectrum of **9a** had peaks at δ 1.25 (OCH_2CH_3), 1.91 ($Se\text{-}CH_3$), 4.15 (benzyl), and 4.40 (OCH_2CH_3), and the IR spectrum had an absorption band of an ester carbonyl group at 1710 cm^{-1}, both in accord with the assigned structure. The ^1H NMR spectrum of **10a** had two quartets at δ 3.63 and 4.38, assigned to two methylene protons of ethoxy groups, and the IR spectrum had an absorption of an ester carbonyl group at 1710 cm^{-1}, also in accord with the assigned structure. When **3** was treated similarly with sodium methoxide in methanol, **2** (8%) and methyl 2-[(methylseleno)methyl]benzoate (**9b**) (13%) were obtained, but methyl 2-(methoxymethyl)benzoate, the analogue of **10a**, was not isolated. On the other hand, **3** was heated in aqueous sodium hydroxide for 10 h under a nitrogen atmosphere to give phthalide (**11**) and 2-(hydroxymethyl)benzoic acid (**10c**) in yields of 12% and 42%, respectively.

The structures of **9** and **10** were confirmed by the alternative synthesis shown in Scheme III. Diselenide **12**[8] was reduced with sodium borohydride and methylated to produce selenide **13**, which was esterified with ethanol in the presence of acid or with diazomethane to give esters **9a,b**, respectively. However, when **13** was treated with methyl iodide in the presence of an alkali in hexamethylphosphortriamide (HMPA), only phthalide (**11**) was formed in 25% yield; ester **9b** was not formed. Phthalide was converted into 2-(chloromethyl)benzoyl chloride (**14**) by treatment with dichlorotriphenylphosphorane;[9] esterification of **14** with ethanol or methanol in the presence of pyridine afforded (chloromethyl)benzoates **15**. Replacement of the chloro group of **15** by reaction with a sodium alkoxide gave esters **10a,b**. Spectral data of the compounds **9** and **10** synthesized by these procedures were identical with those of reaction products of **4**.

The mechanism proposed for the formation of **9** and **10** is shown in Scheme II. An alcohol protonates the C(3) carbanion of the ylide **4** to form a selenonium salt, whose carbonyl carbon is attacked by alkoxide anion. Then the C(3)–C(4) bond cleavage forms a new ylide intermediate **7**. Alcohol protonates the ylide carbanion of **7** to form a selenonium salt **8**. When an alkoxide anion attacks the methyl group of **8** (path a), selenide **9** is formed by demethylation. On the other hand, when the alkoxide anion attacks the benzyl carbon of **8** (path b), dimethyl selenide is eliminated to form **10**. In the case of the reaction in water, the carboxylate anion formed from **8** attacks the benzyl carbon with elimination of dimethyl selenide to form the ring-closure product phthalide (**11**) (path c). Acid **10c** could be formed either by attack of water on the benzylic position of **8** (path b) or by hydrolysis of pathalide (**11**). This reaction mechanism may also apply to the formation of phthalide from **13** and methyl iodide.

Since the selenonium salt **8** is the key intermediate in this scheme, we synthesized **8** and subjected it to thermal treatment in alcohols (Scheme IV). Selenonium salt **8** was derived from **9** by methylation with methyl iodide and silver tetrafluoroborate. Heating **8a** in ethanol afforded **9a** in 14% yield, while heating **8b** in methanol afforded only starting material. On the other hand, treatment of **8a** or **8b** with an equimolar amount of sodium ethoxide in ethanol or with sodium methoxide in methanol gave **9a** (28%) and **10a** (70%), or **9b** (11%) and **10b** (61%), respectively. Thus nucleophilic substitution rather than

(7) The ^{13}C NMR spectrum of *trans*-1,2,3-tribenzoylcyclopropane[4] showed the cyclopropane carbons at δ 30.4 and 36.4 and the ^{13}C NMR of compound **9b** showed the Se-methyl carbon at δ 4.3 and the benzyl carbon at δ 26.9. (See Experimental Section).

(8) Klayman, D. L.; Griffin, T. S. *J. Am Chem. Soc.* **1973**, *95*, 197–199.

(9) Burton, D. J.; Koppes, W. M. *J. Org. Chem.* **1975**, *40*, 3026–3032.

Table II. Reaction of 3 with Acetic Acid

solvent	time (h)	ratio CH_3COOK	ratio CH_3COOH	yield (%) 2	5	6
dichloromethane	8	1	5	29	25	
dichloromethane	8	3	2.5		60	22
acetonitrile	8	1	5	16	13	24

ylide formation by proton abstraction was the main reaction of **8a,b** with alkoxides. The product ratio (**9a**/**10a**) obtained from the reaction of **4** was 1 and that from the reaction of **8a** was 0.4. This result implies that the ylide intermediate **7** forms the demethylated product **9** by a path that does not involve **8**. Treatment of **3** with sodium ethoxide in ethanol at 70 °C to give **9a** (11%) and **10a** (10%), lower yields but approximately the same product ratio that was obtained in refluxing ethanol. This finding indicates that the product ratio **9a**/**10a** does not depend on the reaction temperature but depends on the nucleophilicity of the alcohol toward the selenonium salt **8**. Attempts to react **3** with other alkoxides failed because of the low solubility of **3** in the alcohols.

Reaction of selenonium salt **3** with acetic acid in the presence of potassium acetate gave **2**, **5**, and **6** in varying amounts (Table II). Compounds **5** and **6** were presumably formed via the carbene intermediate as described in Scheme I.

Experimental Section

Melting points were determined on a Yanagimoto micro melting point apparatus and are uncorrected. IR spectra of solids (KBr) and liquids (film or CCl_4 solution) were recorded on a JASCO A-1 spectrophotometer. ^1H NMR spectra were obtained for solutions in $CDCl_3$ on a Hitachi R-20B spectrometer with tetramethylsilane as an internal standard, unless indicated otherwise. ^{13}C NMR spectra were recorded on a JEOL GX-270 spectrometer. Mass spectra were obtained on a JEOL JMS-D300 spectrometer with a direct-insertion probe at 70 eV. Exact mass determination was conducted on the JMA 2000 on-line system. CI-mass spectrum refers to chemical ionization mass spectrometry.

2-Selenochroman-4-one (2). This procedure is the modified method of Renson and Pirson.[3] A solution of 2-(carboxybenzyl)selenoacetic acid (**1**) (20 g, 73 mmol) and potassium acetate (25 g, 255 mmol) in acetic anhydride (94 mL) was refluxed for 2 h and then cooled. Hydrochloric acid solution [prepared from concentrated HCl (25 mL), H_2O (100 mL), and ethanol (100 mL)] was added to the reaction mixture and the resulting solution was heated at 70 °C for 5 h. Most of the solvent was evaporated and dichloromethane was added to the residue. The dichloromethane layer was separated, washed with water and 10% aqueous sodium hydroxide, and dried ($MgSO_4$). Evaporation of the solvent gave an oil which was chromatographed on silica gel (*n*-hexane/dichloromethane = 3:1) to give **2** (11.8 g, 76%).

2-Methyl-4-oxo-2-selenochromanium Tetrafluoroborate (3). Silver tetrafluoroborate (5.1 g, 26 mmol) was added to a solution of **2** (5 g, 24 mmol) and methyl iodide (16.8 g, 120 mmol) in dry dichloromethane (50 mL) and the mixture was stirred at room temperature for 4 h. The precipitate was filtered off and washed with hot acetonitrile. The washings and the filtrate were combined and evaporated. The residual solid was recrystallized from acetonitrile–dichloromethane–ether to give a colorless powder (7.4 g, 100%): mp 112–113 °C; ^1H NMR (CF_3CO_2H) δ 2.80 (3 H, s, CH_3), 4.00–5.22 (4 H, m, $CH_2 \times 2$), 7.35–7.95 (3 H, m, Ar H), 8.10–8.40 (1 H, m, Ar H); IR (KBr) 1060 (BF_4^-), 1640 cm^{-1} (C=O); MS, *m/z* 314 (M^+). Anal. Calcd for $C_{10}H_{11}BF_4OSe$: C, 38.38; H, 3.54. Found: C, 38.18; H, 3.49.

General Procedure for the Thermal Reactions of 2-Methyl-4-oxo-2-selenoniochroman-3-ide (4) in Aprotic Solvents. To a solution of an equimolar quantity of sodium hydride in an aprotic solvent was added selenonium salt **3**. The mixture was stirred at room temperature for 1 h under a nitrogen atmosphere and then refluxed for 12 h. The precipitate (sodium tetrafluoroborate) was filtered off and washed with dichloromethane. The washings and the filtrate were combined and concentrated. The residue was separated by preparative TLC on silica gel (*n*-hexane/dichloromethane = 3:2). The yields of the reactions are shown in Table I.

***(E)*-Bis[2-[(methylseleno)methyl]benzoyl]ethylene (5):** pale yellow needles; mp 113–114 °C; ^1H NMR δ 1.94 (6 H, s, $CH_3 \times 2$), 4.08 (4 H, s, $CH_2 \times 2$), 7.00–7.52 (6 H, m, Ar H), 7.53 (2 H, s, olefin), 7.60–7.86 (4 H, m, Ar H); IR (KBr) 1640 cm^{-1} (C=O); CI-MS (isobutane), *m/z* 453 (MH^+). Anal. Calcd for $C_{20}H_{20}O_2Se_2$: C, 53.35; H, 4.48. Found: C, 53.26; H, 4.45.

***trans*-1,2,3-Tris[2-[(methylseleno)methyl]benzoyl]cyclopropane (6):** brown oil; ^1H NMR δ 1.88, 1.91, 1.95 (each 3 H, each s, CH_3), 3.83–4.14 (7 H, m, CH × 3 and $CH_2 \times 2$), 4.60 (2 H, s, CH_2), 7.22–7.96 (12 H, m, Ar H); ^{13}C NMR δ 4.7, 4.9, 5.0 (CH_3), 25.7, 26.2, 26.4 (CH_2), 34.7, 39.5 (CH), 126.4, 126.7, 126.8, 129.2, 130.4, 130.5, 131.0, 131.2, 131.9, 136.5, 136.8, 137.0, 138.6, 139.8, 145.0, 141.1, 141.2 (aromatic), 195.0, 199.1, 200.3 (C=O); IR (CCl_4 solution) 1660 cm^{-1} (C=O); CI-MS (isobutane) *m/z* 679 (MH^+). Compound **6** gradually decomposed by light.

General Procedure for the Thermal Reactions of 2-Methyl-4-oxo-2-selenoniochroman-3-ide (4) in Protic Solvents. To a solution of an equimolar quantity of sodium hydride in dry alcohol was added selenonium salt **3**. The mixture was stirred at room temperature for 30 min under a nitrogen atmosphere and then refluxed for 6 h. The solvent was evaporated and the residual material was extracted with dichloromethane. The extract was concentrated and the residue was separated by preparative TLC on silica gel (*n*-hexane/dichloromethane = 1:1).

Ethyl 2-[(methylseleno)methyl]benzoate (9a): colorless oil; ^1H NMR δ 1.25 (3 H, t, J = 7.1 Hz, CH_3), 1.91 (3 H, s, $SeCH_3$), 4.15 (2 H, s, CH_2), 4.40 (2 H, q, J = 7.5 Hz, OCH_2), 7.10–7.75 (3 H, m, Ar H), 7.83–8.10 (1 H, m, Ar H); IR (film) 1265, 1710 cm^{-1} (ester); MS, *m/z* 258 (M^+). This sample was identical with an authentic specimen in terms of ^1H NMR, IR, and mass spectra.

Methyl 2-[(methylseleno)methyl]benzoate (9b): colorless oil; ^1H NMR δ 1.92 (3 H, s, $SeCH_3$), 3.90 (3 H, s, OCH_3), 4.19 (2 H, s, CH_2), 7.38–7.55 (3 H, m, Ar H), 7.88–8.10 (1 H, m, Ar H); ^{13}C NMR δ 4.3 ($SeCH_3$), 26.8 (CH_2), 52.0 (OCH_3), 126.7, 130.8, 131.2, 131.7, 141.9 (aromatic), 167.6 (C=O); IR (film) 1260, 1720 cm^{-1} (ester); MS, *m/z* 244 (M^+). This sample was identical with an authentic specimen in terms of ^1H NMR, IR, and mass spectra.

Ethyl 2-(ethoxymethyl)benzoate (10a): colorless oil; ^1H NMR δ 1.37 (3 H, t, J = 6 Hz, OCH_2CH_3), 1.90 (3 H, t, J = 7 Hz, $CO_2CH_2CH_3$), 3.63 (2 H, q, J = 6 Hz, OCH_2CH_3), 4.38 (2 H, q, J = 7 Hz, $CO_2CH_2CH_3$), 4.91 (2 H, s, CH_2Ph), 7.20–8.10 (4 H, m, Ar H); IR (film) 1250, 1710 cm^{-1} (ester); MS, *m/z* 208 (M^+). This sample was identical with an authentic specimen in terms of ^1H NMR, IR, and mass spectra.

2-[(Methylseleno)methyl]benzoic Acid (13). To a solution of α,α'-diselenodi-*o*-toluic acid (**12**)[8] (2 g, 4.7 mmol) and sodium hydroxide (0.4 g, 10 mmol) in dry ethanol (60 mL) was added sodium borohydride (0.5 g, 13 mmol) gradually at room temperature, and the mixture was stirred for 15 min. Methyl iodide (2 g, 14 mmol) was added at 0 °C to the solution. The resulting mixture was stirred for 30 min, poured into water, and acidified. The copious white precipitate was suction-filtered and dried in vacuo. Recrystallization from ether–*n*-hexane gave a colorless powder (1.8 g, 83%): mp 150–151 °C (lit.[10] mp 164 °C); ^1H NMR (Me_2SO-d_6) δ 1.88 (3 H, s, CH_3), 4.17 (2 H, s, CH_2), 7.20–7.60 (3 H, m, Ar H), 7.84–8.08 (1 H, m, Ar H); IR (KBr) 1678 cm^{-1} (C=O); MS, *m/z* 230 (M^+). Anal. Calcd for $C_9H_{10}O_2Se$: C, 47.18; H, 4.40. Found: C, 47.22; H, 4.35. The spectral data of **13** were identical with those of a sample by Renson et al.[10]

Ethyl 2-[(Methylseleno)methyl]benzoate (9a). A mixture of **13** (1.0 g, 4.4 mmol), dry ethanol (2.0 g, 44 mmol), 3A molecular sieves (0.5 g), and sulfuric acid (3 drops) in benzene (10 mL) was refluxed for 10 h. The cooled mixture was filtered. The filtrate was washed with saturated aqueous sodium bicarbonate and dried ($MgSO_4$). The solvent was evaporated and the residue was chromatographed on silica gel (*n*-hexane/dichloromethane = 3:2) to give a colorless oil (220 mg, 19%). High resolution MS: calcd for $C_{11}H_{14}O_2Se$ *m/z* 258.0167, found *m/z* 258.0168.

Methyl 2-[(Methylseleno)methyl]benzoate (9b). Nitrosomethylurea (300 mg, 2.9 mmol) was gradually added to a mixture

(10) Loth-Compere, M.; Luxen, A.; Thibaut, Ph.; Christiaens, L.; Guillaume, M.; Renson, M. *J. Heterocycl. Chem.* **1981**, *18*, 343–345.

of 50% aqueous potassium hydroxide (3 mL) and ether (5 mL) below 5 °C. Diazomethane in ether thus prepared was gradually added to a suspension of **13** (350 mg, 1.5 mmol) in ether (20 mL) at 0 °C and the mixture stirred for 1.5 h. The solution was concentrated and the residue was subjected to preparative TLC on silica gel (*n*-hexane/dichloromethane = 1:1) to give a colorless oil (304 mg, 82%). High resolution MS: calcd for $C_{10}H_{12}O_2Se$ m/z 244.0002, found m/z 244.0005.

General Procedure for Preparing Alkyl 2-(Chloromethyl)benzoates 15a,b. To a solution of pyridine (1 g, 13 mmol) in dry alcohol (10 mL) was added crude **14**[9] (~10 mmol) gradually at 0 °C over 10 min, and the mixture was stirred at room temperature for 18 h. Then 3 N hydrochloric acid was added to the solution. An oil separated and was extracted with ether. The ether layer was washed with water and dried ($MgSO_4$). The solvent was evaporated and the residue was chromatographed on silica gel (*n*-hexane/dichloromethane = 10:1).

Ethyl 2-(chloromethyl)benzoate (15a): 53% (overall yield from **11**); colorless oil; ^1H NMR δ 1.40 (3 H, t, J = 6.7 Hz, CH_3), 4.40 (2 H, q, J = 6.0 Hz, CH_2CH_3), 5.05 (2 H, s, $ArCH_2Cl$), 7.25–7.63 (3 H, m, Ar H), 7.75–8.10 (1 H, m, Ar H); IR (film) 1280, 1720 cm^{-1} (ester); high resolution MS, calcd for $C_{10}H_{11}ClO_2$ m/z 198.0448, found m/z 198.0473.

Methyl 2-(chloromethyl)benzoate (15b): 58% (overall yield from **11**); colorless oil; ^1H NMR δ 3.93 (3 H, s, CH_3), 5.05 (2 H, s, CH_2), 7.25–7.65 (3 H, m, Ar H), 7.80–8.10 (1 H, m, Ar H); IR (film) 1285, 1720 cm^{-1} (ester); high resolution MS, calcd for $C_9H_9ClO_2$ m/z 184.0291, found m/z 184.0281.

General Procedure for Preparing Alkyl 2-(Alkoxymethyl)benzoates 10a,b. To a solution of **15a,b** (500 mg) in dry alcohol (20 mL) was added an equimolar quantity of sodium hydride. The mixture was refluxed for 4 h and evaporated. The residue was chromatographed on silica gel (*n*-hexane/dichloromethane = 3:1).

Ethyl 2-(ethoxymethyl)benzoate (10a) (82%): high resolution MS, calcd for $C_{12}H_{16}O_3$ m/z 208.1099, found m/z 208.1073.

Methyl 2-(methoxymethyl)benzoate (10b) (85%): colorless oil; ^1H NMR δ 3.45 (3 H, s, OCH_3), 3.83 (3 H, s, CO_2CH_3), 4.82 (2 H, s, CH_2), 7.25–8.13 (4 H, m, Ar H); IR (film) 1260, 1720 cm^{-1} (ester); high resolution MS, calcd for $C_{10}H_{12}O_3$ m/z 180.0786, found m/z 180.0783.

General Procedure for Preparing [2-(Alkoxycarbonyl)benzyl]dimethylselenonium Tetrafluoroborates 8a,b. To a solution of **9a,b** (200 mg) in dry dichloromethane (10 mL) was added 5 molar equiv of methyl iodide at 0 °C and the mixture was stirred for 15 min. Then 1.1 molar equiv of silver tetrafluoroborate was added and the mixture was stirred at room temperature for 30 min. The precipitate was filtered off and washed with dry dichloromethane. The washings and filtrate were combined and ether was added to the solution. The precipitate was filtered off and recrystallized from acetonitrile–*n*-hexane.

[2-(Ethoxycarbonyl)benzyl]dimethylselenonium tetrafluoroborate (8a) (82%): colorless powder (254 mg, 82%); mp 125–126 °C; ^1H NMR (CF_3CO_2H) δ 1.54 (3 H, t, J = 7 Hz, CH_2CH_3), 2.82 (6 H, s, $CH_3 \times 2$), 4.56 (2 H, q, J = 7 Hz, CH_2CH_3), 4.95 (2 H, s, CH_2Ph), 7.50–7.90 (3 H, m, Ar H), 8.23–8.48 (1 H, m, Ar H); IR (KBr) 1060 (BF_4^-), 1272, 1710 cm^{-1} (ester). Anal. Calcd for $C_{12}H_{17}BF_4O_2Se$: C, 40.17; H, 4.77. Found: C, 39.99; H, 4.70.

[2-(Methoxycarbonyl)benzyl]dimethylselenonium tetrafluoroborate (8b) (87%): colorless powder; mp 140–141 °C; ^1H NMR (CF_3CO_2H) δ 2.83 (6 H, s, $CH_3 \times 2$), 4.10 (3 H, s, OCH_3), 4.92 (2 H, s, benzyl), 7.47–7.90 (3 H, m, Ar H), 8.20–8.45 (1 H, m, Ar H); IR (KBr) 1070 (BF_4^-), 1270, 1710 cm^{-1} (ester). Anal. Calcd for $C_{11}H_{15}BF_4O_2Se$: C, 38.30; H, 4.38. Found: C, 38.02; H, 4.28.

General Procedure for the Thermal Reactions of 8a,b in Alcohols. A suspension of **8a,b** (100 mg) in a dry alcohol (5 mL) was refluxed for 8 h under a nitrogen atmosphere. The solvent was evaporated and the residue was separated by preparative TLC on silica gel (*n*-hexane/dichloromethane = 3:2). The product **9a** was obtained from **8a** in 14% yield and the starting selenonium salt **8b** was recovered by the reaction of **8b** in methanol. All products were identical with authentic specimens in terms of ^1H NMR and IR spectra.

General Procedure for the Reactions of 8a,b with Sodium Alkoxide. The selenonium salt **8a,b** (100 mg) was added to an alkoxide solution prepared from an equimolar amount of sodium hydride in an alcohol (5 mL). The mixture was stirred at room temperature for 1.5 h under a nitrogen atmosphere and then refluxed for 5 h. The solvent was evaporated and the residue was separated by preparative TLC on silica gel (*n*-hexane/dichloromethane = 3:2). The products **9a** and **10a** were obtained from **8a** in yields of 28% and 70%, respectively, and the corresponding methyl derivatives **9b** and **10b** were obtained from **8b** in yields of 11% and 61%, respectively. All products were identical with authentic specimens in terms of ^1H NMR and IR spectra.

Thermal Reaction of 4 in Water. Selenonium salt **3** (313 mg, 1 mmol) was added to a solution of sodium hydroxide (220 mg, 5.5 mmol) in distilled water (10 mL). The mixture was stirred at room temperature for 1 h and then refluxed for 10 h under a nitrogen atmosphere. The cooled solution was acidified with hydrochloric acid. The precipitate was filtrated, washed with dichloromethane, and dried in vacuo to give 2-(hydroxymethyl)benzoic acid (**10c**) (64 mg, 42%). The filtrate was extracted with dichloromethane. The extract was washed with water, combined with the washings, and dried ($MgSO_4$). The solvent was evaporated and the residue was separated by preparative TLC on silica gel (benzene/acetone = 10:1) to give phthalide (**11**) (16 mg, 12%). All products were identical with authentic specimens in terms of ^1H NMR and IR spectra.

Reaction of 13 with Methyl Iodide in HMPA. To a solution of **13** (290 mg, 1.3 mmol) in HMPA (5 mL) were added sodium hydroxide (79 mg), water (0.3 mL), and methyl iodide (725 mg, 5.1 mmol), and the mixture was stirred at room temperature for 3 h. The solution was poured into water (30 mL), acidified with hydrochloric acid, and extracted with ether. The ether extract was washed with water and saturated aqueous sodium chloride and then dried ($MgSO_4$). The solvent was evaporated and the residue was separated by preparative TLC on silica gel (*n*-hexane/dichloromethane = 3:2) to give **11** (50 mg, 25%). This sample was identical with an authentic specimen in terms of ^1H NMR and IR spectra.

Reactions of 4 with Acetic Acid. To a suspension of **3** (625 mg, 2 mmol) in dichloromethane or acetonitrile (15 mL) was added anhydrous potassium acetate, and the mixture was stirred at room temperature for 1.5 h under a nitrogen atmosphere. Then acetic acid was added to the mixture. The resulting mixture was refluxed for 8 h, cooled, poured into water, and extracted with dichloromethane. The dichloromethane extract was washed with water and saturated aqueous sodium bicarbonate and dried ($MgSO_4$). The solvent was evaporated and the residue was separated by preparative TLC on silica gel (*n*-hexane/dichloromethane = 3:2). The solvent, reaction conditions, and yields are shown in Table II. All products were identical with authentic specimens in terms of ^1H NMR and IR spectra.