Synthesis and Reactions of 10-Chloro-10,9-(epoxyalkano)selenoxanthenes and 1-Chloro-1-phenyl-3*H*-2,1-benzoxaselenoles

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10-Chloro-10,9-(epoxyalkano)selenoxanthenes (12, 14—17) were prepared by the reaction of 9-(hydroxyalkyl)-selenoxanthenes (4, 9—11) with *N*-chlorosuccinimide, and 1-chloro-1-phenyl-3*H*-2,1-benzoxaselenoles (32—34) were similarly synthesized. The selenurane structure of 14 was established by X-ray analysis. The proton nuclear magnetic resonance and electron impact mass spectral data supported the selenurane structures of these compounds.

Reactions of the selenurane 16 with sodium acetylacetonide gave a selenoxantheniomethanide derivative 37. Thermal reaction of 14 provided 9-(1-chloro-2-hydroxyethylidene)selenoxanthene (41) together with 9-(2-hydroxyethyl)selenoxanthene (9), while thermal reaction in ethanol produced 9-(1-chloro-2-hydroxyethyl)-9-ethoxyselenoxanthene (42). On the other hand, the benzoxaselenole selenurane (32) was heated at 195—200 °C to afford 2-(phenylseleno)benzyl chloride (45), 2-(phenylseleno)benzyl 2-(phenylseleno)benzoate (46) and 2-(phenylseleno)benzaldehyde (28).

Keywords selenurane; selenonium salt; selenoxanthene; 3*H*-2,1-benzoxaselenole; thermal reaction; hydrolysis; X-ray analysis

In selenuranes the selenium atom has a valence shell of ten electrons. These compounds are usually classified as σ- and π-selenuranes depending upon whether four of the five valence electron pairs of the selenium atom form four σ-bonds or three σ-bonds and a π-bond to the neighboring elements. We previously reported on the chemistry of some π-selenuranes (selenonium ylides[1] and selenilimines[2]). σ-Selenuranes so far isolated possess strongly electron-attracting groups in the apical positions[3] and are five-membered spiro compounds with a spiro selenium atom.[4]

We report here syntheses and reactions of some selenoxanthene selenuranes, in which an epoxyalkano group forms a bridge between C-9 and the selenium atom, and some benzoxaselenole selenuranes.[5]

Syntheses of σ-Selenuranes Chart 1 shows a synthetic scheme for 9-hydroxymethyl- and 9-hydroxyethylselenoxanthenes. Selenoxanthene (**1**) was lithiated with *n*-butyllithium followed by carbonation with dry ice to give selenoxanthene-9-carboxylic acid (**2**) in 74.6% yield. Esterification of the carboxylic acid **2** afforded and ethyl ester **3** and reduction of **3** with lithium aluminum hydride (LAH) gave 9-hydroxymethylselenoxanthene (**4**) in 92.2% yield. 9-Methylselenoxanthene (**6**) was derived from selenoxanthylium salt (**5**) and methylmagnesium iodide in 52.1% yield, together with a dimeric product, 9,9-biselenoxanthenyl (**7**). In order to avoid the production of the dimer **7**, an alternative procedure was employed: methylation of the selenoxanthenide anion generated from **1** and *n*-butyllithium afforded the selenoxanthene **6**, quantitatively. 9-Hydroxyethylselenoxanthenes (**9**—**11**) were prepared by the reaction of carbanions of the selenoxanthenes **1**, **6**, **8** with oxirane in good yields.

Synthetic procedures for selenoxanthene selenuranes and the corresponding selenoxanthenium salts are shown in Chart 2. 10-Chloro- or 10-bromo-10,9-(epoxyalkano)-selenoxanthenes (**12**,**14**—**17**) were obtained by treatment of 9-(hydroxyalkyl)selenoxanthenes (**4**, **9**—**11**) with *N*-chlorosuccinimide (NCS) or *N*-bromosuccinimide (NBS) and the corresponding selenonium perchlorates (**18**—**20**) were prepared from the selenuranes (**14**—**16**) and silver perchlorate. However, the selenurane **12** did not produce the selenonium salt (**13**) but selenoxanthylium salt (**5**), which would be formed by decarbonylation of **13**. We attempted to synthesize a selenurane (**22**) possessing a carboxyl bridge, but the selenurane **22** readily decarboxylated to form the 9-phenylselenoxanthylium salt (**24**), which was led to 9-methoxy-9-phenylselenoxanthene (**25**) and 9-phenylselenoxanthen-9-ol (**26**) by treatment with sodium methoxide. An oxygen-bridged selenurane **27** was prepared from **26** and NCS.

Next, we synthesized the benzoxaselenole selenuranes in order to compare their stability and reactivity with those of

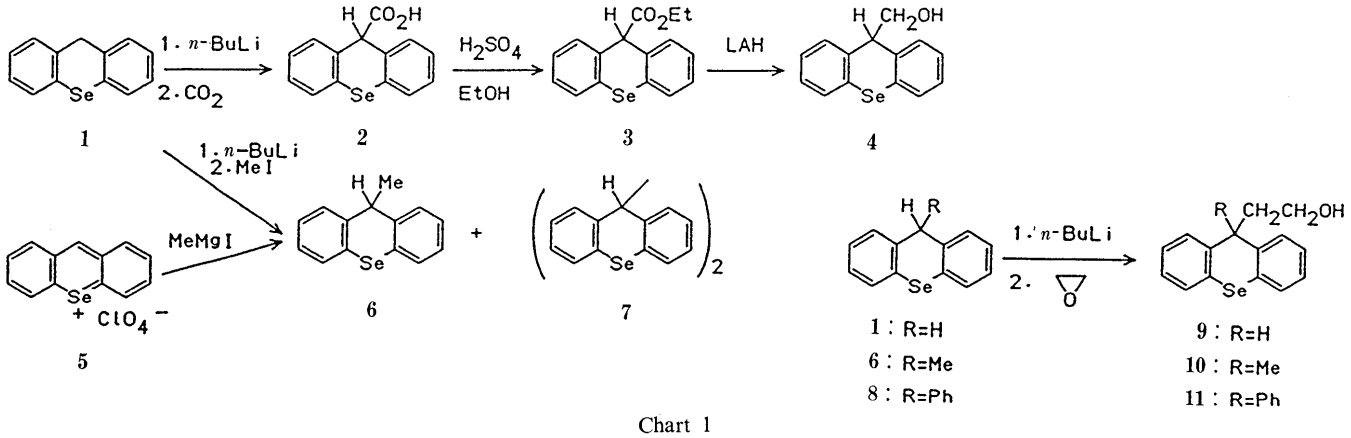

Chart 1

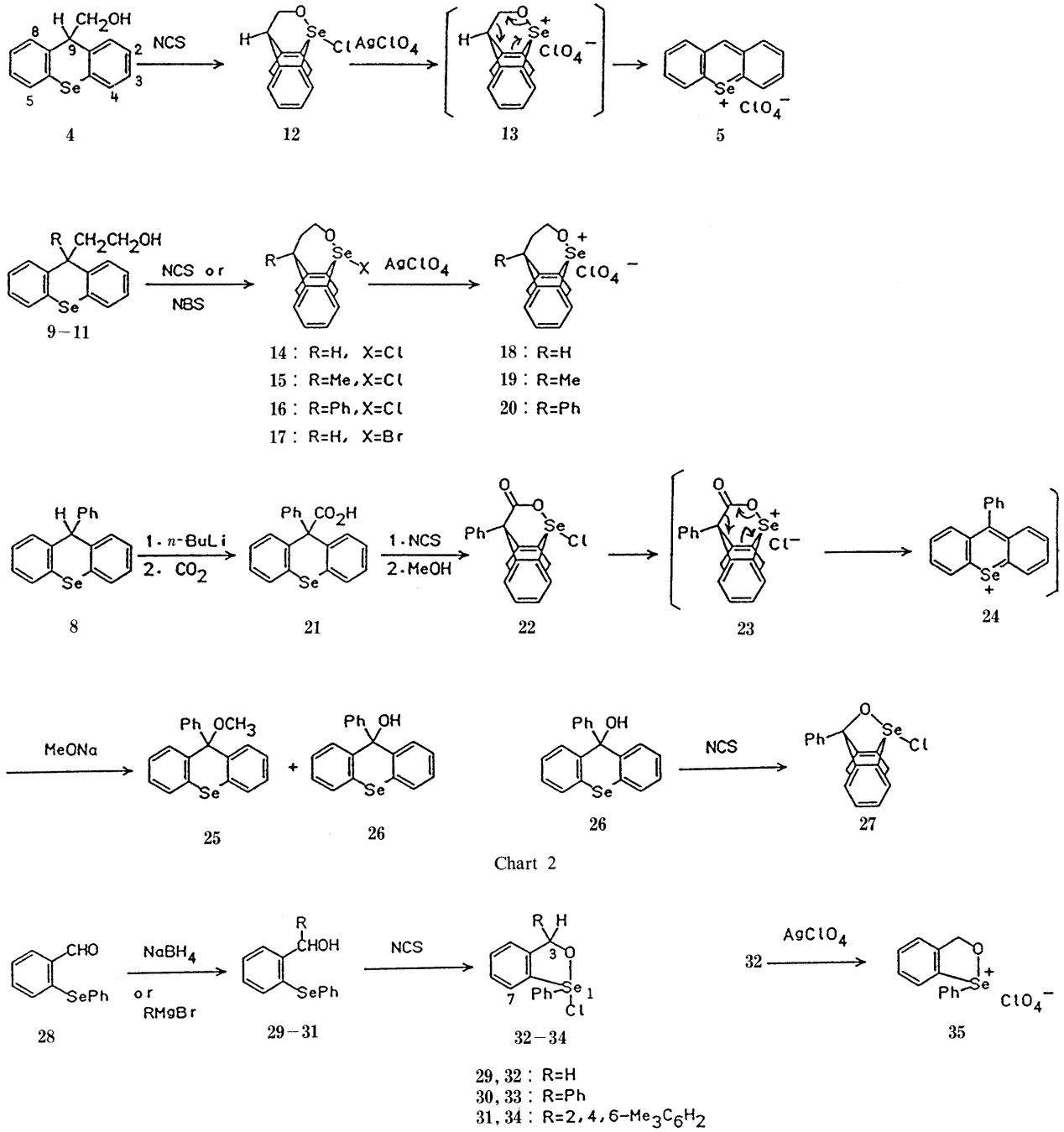

Chart 2

Chart 3

the selenoxanthene selenuranes (**14**—**17**, **27**). Reduction of 2-(phenylseleno)benzaldehyde (**28**) with sodium borohydride afforded a benzyl alcohol **29** in a quantitative yield. The Grignard reactions of **28** gave the selenobenzhydryl alcohols **30**, **31**. The selenoalcohol derivatives **29**—**31** were chlorinated with NCS to give 1-chloro-1-phenyl-3*H*-2,1-benzoxaselenoles (**32**—**34**) in high yields. The selenurane **32** was treated with silver perchlorate to afford the selenonium salt **35**.

Spectral Data of σ-Selenuranes Next, we will discuss the hypervalent bonds of the selenuranes synthesized above on the basis of their ^{1}H-nuclear magnetic resonance (^{1}H-NMR) spectra. The H-7 signals of benzoxaselenole selenuranes **32**—**34** appeared at very low field (δ 8.80—9.20), whereas that of the selenonium salt **35** appeared at δ 8.1—8.3. The *gem*-methylene coupling constant of the bridged methylene group (J=13.8 Hz) of **32** is considerably larger than that of **35**. These phenomena have been observed in the five-membered monocyclic selenuranes and have been attributed to the covalent nature of the apical bonds.[6] On the other hand, the H-4,5 signals of selenoxanthene selenuranes **12**, **14**—**17**, **27** were observed at δ 8.23—8.60 and were at lower field than those of the selenonium salts **18**—**20** (δ 8.10—8.40). Those lowfield shifts in the selenoxanthene selenuranes are not as large as those of the benzoxaselenole selenuranes mentioned above. This difference can be explained by the stereostructural assumption that the Se–Cl bond and the *ortho*-proton–C(Ar) bond are parallel in the benzoxaselenole selenuranes and are not parallel in the selenoxanthene selenuranes (see the X-ray structure analysis). Therefore, the anisotropic effect of the apical Se–Cl bond is exerted more strongly

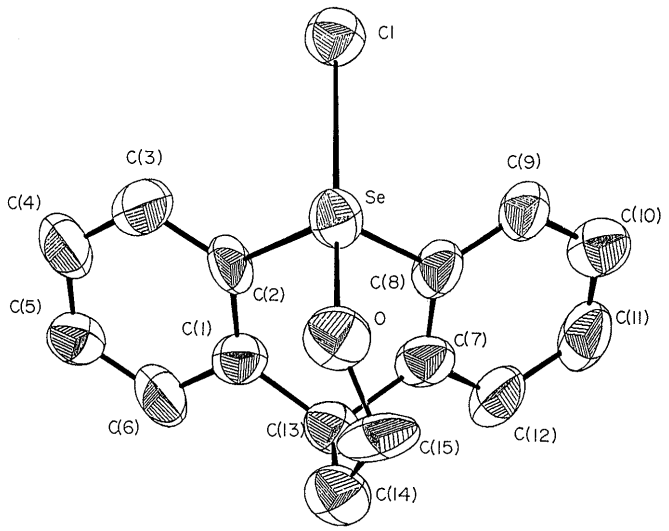

Fig. 1. X-Ray Structure of the Selenurne **14**

TABLE I. Atomic Coordinates ($\times 10^4$) for Non-hydrogen Atoms and Equivalent Thermal Parameters of **14**

Atom	x	y	z	B_{eq}[a)]
Se	422.0 (7)	3023 (1)	907.8 (8)	4.9
Cl	985 (2)	5574 (3)	859 (2)	6.0
O	6 (5)	1315 (8)	935 (6)	6.7
C(1)	1559 (7)	1516 (11)	230 (8)	5.0
C(2)	1021 (6)	2549 (12)	10 (7)	4.3
C(3)	881 (7)	3144 (12)	−893 (9)	5.8
C(4)	1280 (8)	2710 (13)	−1555 (8)	5.9
C(5)	1815 (8)	1712 (12)	−1319 (8)	5.8
C(6)	1960 (7)	1109 (12)	−448 (8)	5.8
C(7)	1703 (7)	1730 (11)	2026 (8)	5.2
C(8)	1174 (7)	2757 (12)	2014 (7)	4.8
C(9)	1124 (7)	3571 (12)	2803 (8)	5.1
C(10)	1634 (7)	3366 (12)	3610 (9)	6.0
C(11)	2181 (8)	2402 (13)	3606 (8)	6.3
C(12)	2246 (7)	1541 (12)	2816 (8)	5.4
C(13)	1698 (7)	763 (12)	1183 (8)	5.7
C(14)	1084 (8)	−340 (13)	1195 (9)	7.0
C(15)	360 (8)	188 (12)	1448 (11)	8.0

a) Equivalent isotropic thermal parameters were calculated from the refined anisotropic thermal parameters.

on H-7 of the benzoxaselenole selenuranes than on H-4,5 of the selenoxanthene selenuranes.

The selenuranes **14**—**17** showed the molecular ion peaks (M^+) but the corresponding selenonium salts **18**—**20** did not show M^+ in the electron-impact mass spectra (EI-MS). On the other hand, the benzoxaselenole selenuranes **32**—**34** did not exhibit M^+ but did show $M^+ - 1$ in the EI-MS, probably because they lose H-3 to form the stable radical cation.

X-Ray Structure of Selenurane 14 The hypervalent structure of 10-chloro-10,9-epoxyethanoselenoxanthene (**14**) was confirmed by the X-ray structure determination. Figure 1 shows the molecular structure of **14**. Atomic coordinates are listed in Table I and bond distances and bond angles are summarized in Table II.

The geometry about selenium is a slightly distorted trigonal bipyramid. The selenoxanthene constitutes two equatorial ligands and the third equatorial position is occupied by the selenium lone pair. The chlorine and oxygen ligands occupy the two apical positions. The

TABLE II. Bond Distances (Å) and Angles (°) for Non-hydrogen Atoms of **14** with Their e.s.d.'s in Parentheses

Se–Cl	2.761 (3)	Se–O	1.878 (9)
Se–C(2)	1.97 (1)	Se–C(8)	1.97 (1)
O–C(15)	1.45 (2)	C(1)–C(2)	1.44 (2)
C(1)–C(6)	1.43 (2)	C(1)–C(13)	1.59 (2)
C(2)–C(3)	1.45 (2)	C(3)–C(4)	1.42 (2)
C(4)–C(5)	1.41 (2)	C(5)–C(6)	1.41 (2)
C(7)–C(8)	1.42 (2)	C(7)–C(12)	1.42 (2)
C(7)–C(13)	1.59 (2)	C(8)–C(9)	1.45 (2)
C(9)–C(10)	1.40 (2)	C(10)–C(11)	1.41 (2)
C(11)–C(12)	1.49 (2)	C(13)–C(14)	1.60 (2)
C(14)–C(15)	1.57 (2)		
Cl–Se–O	178.0 (3)	Cl–Se–C(2)	86.1 (3)
Cl–Se–C(8)	86.1 (4)	O–Se–C(2)	95.3 (4)
O–Se–C(8)	95.3 (4)	C(2)–Se–C(8)	97.5 (5)
Se–O–C(15)	124.5 (8)	C(2)–C(1)–C(6)	119 (1)
C(2)–C(1)–C(13)	122 (1)	C(6)–C(1)–C(13)	119 (1)
Se–C(2)–C(1)	119.0 (8)	Se–C(2)–C(3)	120.9 (8)
C(1)–C(2)–C(3)	120 (1)	C(2)–C(3)–C(4)	120 (1)
C(3)–C(4)–C(5)	119 (1)	C(4)–C(5)–C(6)	122 (1)
C(1)–C(6)–C(5)	120 (1)	C(8)–C(7)–C)12)	119 (1)
C(8)–C(7)–C(13)	122 (1)	C(12)–C(7)–C(13)	118 (1)
Se–C(8)–C(7)	119.3 (9)	Se–C(8)–C(9)	117.3 (8)
C(7)–C(8)–C(9)	123 (1)	C(8)–C(9)–C(10)	119 (1)
C(10)–C(11)–C(12)	125 (1)	C(7)–C(12)–C(11)	116 (1)
C(1)–C(13)–C(7)	114 (1)	C(1)–C(13)–C(14)	110 (1)
C(7)–C(13)–C(14)	108 (1)	C(13)–C(14)–C(15)	116 (1)
O–C(15)–C(14)	117 (1)		

Cl–Se–O bond angle (178.0°) is nearer colinearity than in any other cyclic selenurane yet studied.[7] The Se–Cl bond length for **14** (2.761 Å) is significantly longer than the sum of the selenium and chlorine covalent radii (2.16 Å) and the Se–O bond length is slightly longer than that of tetra-alkoxy selenurane.[4b] One of the condensed benzene rings is deformed: the bond length between C(11) and C(12) (1.49 Å) is significantly longer than any other C–C bond of the benzene rings and the bond angle of C(10)–C(11)–C(12) is wider. The reason for these abnormal values is unclear.

Reactions of σ-Selenuranes Chart 4 shows reactions of the selenoxanthene selenuranes **14**, **16**, **27**.

Reactions of **27** and **16** with sodium acetylacetonide afforded (selenoxanthen-10-io)diacetylmethanides **36** and **37** in high yields, respectively. The stereochemistry of these ylides was determined from the ^{1}H-NMR spectra. If the hydroxyl group of **36** occupies the pseudo-equatorial (e′) position, a lowfield shift of H-1,8 is observed at near δ 8.0. However, a highfield shift of H-1,8 appeared at δ 7.10—7.22, and this is attributable to the anisotropic effect of the e′-phenyl group. Namely, the hydroxyl group at C-9 is pseudo-axial (a′). The H-1,8 signal of **37** appeared at δ 6.68—6.91, at higher field than that of **36**. This shows that the 9-phenyl group lies in the e′ position. From a Dreiding model study, the diacetylmethanide group of both ylides (**36** and **37**) occupies the e′ position because of the steric repulsion by the 9-a′-hydroxyl or 9-a′-hydroxyethyl group.

Treatment of the selenuranes **14** and **16** with 10% sodium hydroxide afforded 9-(2-hydroxyethyl)selenoxanthene 10-oxides **38** and **39** in high yields, respectively. It should be noted that **16** was also hydrolyzed during thin layer chromatography (TLC). The infrared (IR) spectra of **38** and **39** exhibited the absorption bands of a hydroxyl group at

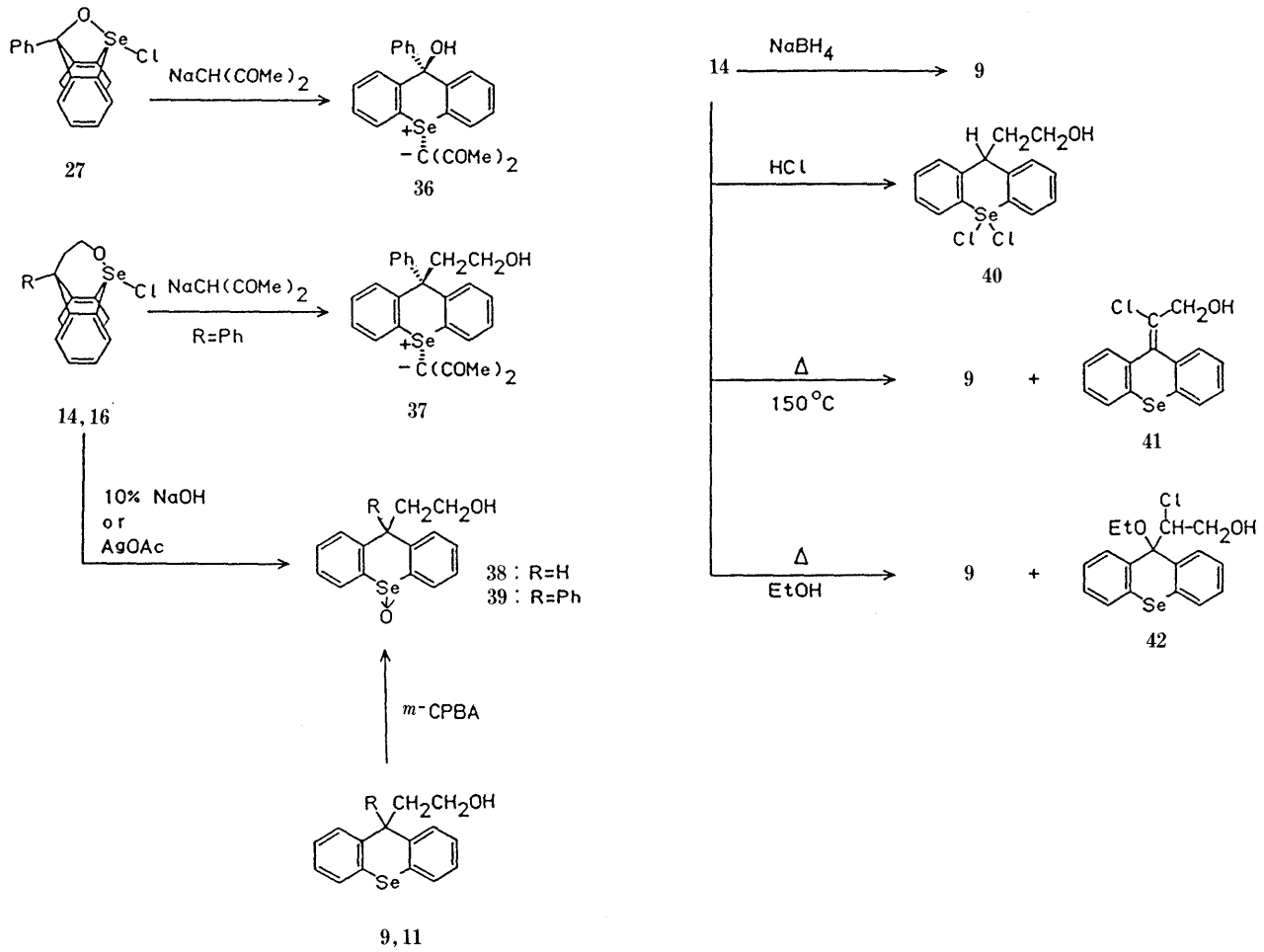

Chart 4

3200 cm^{-1} and a selenoxide group at 820 cm^{-1}. Their structures were estimated to be selenoxide-alcohols. Authentic samples of **38** and **39** were prepared by oxidation of the selenide-alcohols **9** and **11** with *m*-chloroperbenzoic acid (*m*-CPBA), respectively. Product **39** was a mixture of *E*- and *Z*-isomers and their stereostructures were determined from the ^{1}H-NMR spectrum. Since the ^{1}H-NMR spectrum showed highfield-shifted signals due to H-1,8 at δ 6.81, the phenyl group and the hydroxyethyl group at 9-position occupy e′ and a′ positions, respectively. The *E*-isomer has a *cis*-relationship between the seleninyl group and the hydroxyethyl group. Therefore, the methylene group of the hydroxyethyl moiety are affected by the anisotropic effect of the seleninyl group and the methylene signals are shifted downfield: 0.48 ppm for the 1′-methylene group and 0.22 ppm for the 2′-one. In the *Z*-isomer H-4,5 were influenced by the e′-seleninyl group and the signal was observed at δ 7.95. The isomer ratio ($Z/E=6/5$) was calculated from the signal intensities of the methylene groups. The ^{1}H-NMR spectrum of **38** showed a downfield-shifted multiplet due to H-4,5 at δ 8.02—8.10 and a doublet of triplets due to the 1′-methylene group was shifted upfield from that of the *Z*-isomer of **39**. On the basis of this spectral evidence, the selenoxide **38** has the *E*-configuration with the e′-seleninyl group and the a′-hydroxyethyl group. It is known that selenoxides change their stereochemistry through selenuranes formed by addition of water[8] and this phenomenon has been observed in the selenoxanthene selenoxides.[2] Therefore the stereochemistry of the selenoxide formation from selenuranes **14** and **16** by hydroxide ion cannot be discussed. Substitution of the chlorine atom with acetate ion was attempted by the reaction of **14** with silver acetate but only the hydrolysis product **38** was formed.

Reduction of **14** with sodium borohydride afforded 9-(2-hydroxyethyl)selenoxanthene (**9**) in quantitative yield, and reaction with hydrogen chloride gave 9-(2-hydroxyethyl)-selenoxanthene dichloride (**40**). When **14** was heated at 150 °C for 10 min, 9-(1-chloro-2-hydroxyethylidene)selenoxanthene (**41**) was formed in 27.6% yield together with **9** (30.4%). The structure of the product **41** was determined on the basis of its spectral data: an absorption band of the hydroxyl group at 3130 cm^{-1} in the IR spectrum, a pair of double doublets of the methylene group at δ 4.36 and 4.50 in the ^{1}H-NMR spectrum and two signals of tetra-substituted olefinic carbons at δ 135.78 and 137.85 in the ^{13}C-NMR spectrum. Thermal reaction of the selenurane **14** in ethanol gave 9-ethoxy-9-(1-chloro-2-hydroxyethyl)-selenoxanthene (**42**) in 42.1% yield. The IR spectrum of **42** exhibited an absorption band of the hydroxyl group at 3470 cm^{-1}. The ^{1}H-NMR spectrum indicates the presence of the $CH(Cl)CH_2OH$ moiety on the basis of signals at δ 2.54 (dd, $J=8.8$, 3.9 Hz) of OH, 3.61 (ddd, $J=7.3$, 8.8, 12.2 Hz) and 3.80 (ddd, $J=3.9$, 3.9, 12.2 Hz) of CH_2O and 4.33 (dd, $J=7.3$, 3.9 Hz) of CHCl. The ^{13}C-NMR spectrum showed the carbon signals of CH_2OH, CHCl and C-9 at δ 63.2, 70.8, and 83.5, respectively. Although these thermal reactions are unique and interest-

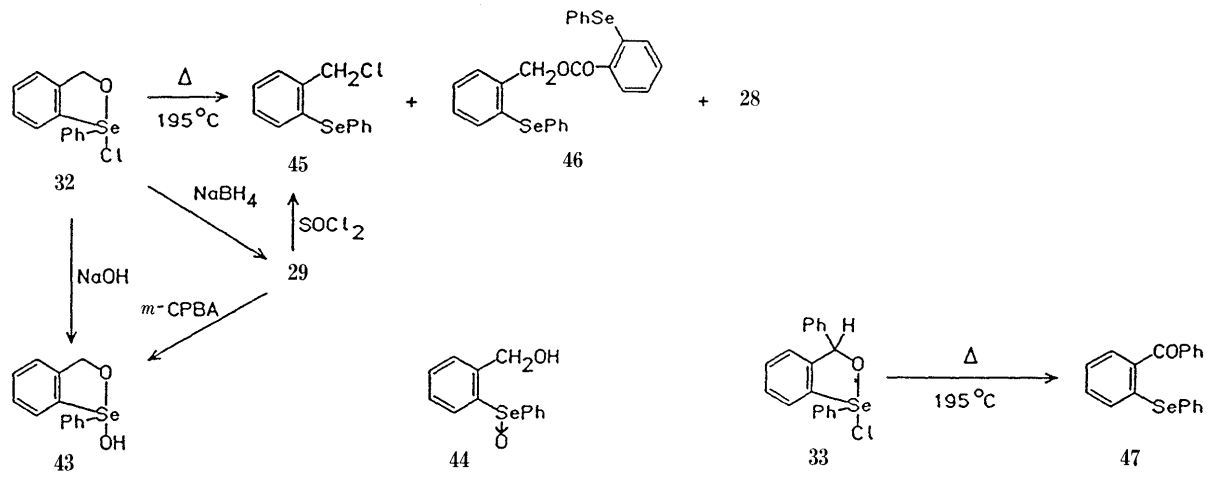

Chart 5

ing, we cannot yet explain the reaction mechanism. In order to elucidate the reaction pathways we intend to prepare other *Se*-chloro-*Se*-alkoxyselenuranes and examine their thermal reactions in the near future.

Reduction of the benzoxaselenole selenurane **32** with sodium borohydride afforded 2-phenylselenobenzyl alcohol (**29**) in 90.7% yield and hydrolysis with sodium hydroxide gave 1-hydroxy-1-phenyl-3*H*-2,1-benzoxaselenole (**43**) in 96.1% yield. The IR spectrum of the product **43** had no absorption band of the selenoxide at ca. 820 cm^{-1}. In the ^{1}H-NMR spectrum a characteristic signal of H-7 of the benzoxaselenole selenurane appeared separately at a downfield position (δ 7.95—8.30) and the *gem*-coupling constant of the benzylic methylene (J = 13.8 Hz) is the same as that of the chloroselenurane **32**. The ^{1}H-NMR spectral evidence is very similar to that of 1-methoxybenzoxaselenole selenurane.[4a] On the basis of these spectral data, the product **43** would be the benzoxaselenole selenurane rather than 2-hydroxyphenyl phenyl selenoxide (**44**). The selenurane **43** was alternatively synthesized by oxidation of 2-phenylselenobenzyl alcohol (**29**) with *m*-CPBA.

The selenurane **32** was heated at 195—200 °C under a nitrogen atmosphere to form 2-(phenylseleno)benzaldehyde (**28**), 2-(phenylseleno)benzyl chloride (**45**) and 2-(phenylseleno)benzyl 2-(phenylseleno)benzoate (**46**) in 21.8%, 23.8% and 12.5% yields, respectively. The structure of the ester **46** was determined from the results of elemental analysis and spectral data. Elemental analysis and MS showing the molecular ion peak at *m/z* 524 indicate a molecular formula of $C_{26}H_{20}O_2Se_2$, corresponding to **46**. The IR spectrum showed an absorption band due to the carbonyl group at 1703 cm^{-1}. In the ^{1}H-NMR spectrum, a methylene group appeared as a singlet at δ 5.57, aromatic protons as multiplets at δ 6.8—7.85 and an *ortho* proton to the carbonyl group at δ 7.9—8.1 as a multiplet. Other products, **28** and **45**, were identified by comparison with authentic samples. The formation mechanism of the ester **46** is not clear so far. Thermal reaction of the 3-phenyl derivative **33** afforded 2-(phenylseleno)benzophenone (**47**) in 74.5% yield. The product **47** was identified by comparison with an authentic sample.

Experimental

All melting points were determined on a Yanagimoto micro melting point apparatus and are uncorrected. IR spectra were recorded on a JASCO IRA-1 spectrometer. ^{1}H-NMR spectra were measured on Hitachi R-24 (60 MHz), JEOL FX-200 (200 MHz) and JEOL GX-270 (270 MHz) spectrometers and ^{13}C-NMR spectra were recorded on a JEOL GX-270 spectrometer with tetramethylsilane as an internal standard. MS were measured on a JEOL D-300 spectrometer and high-resolution MS were taken on a JMA-2000 on-line system.

Selenoxanthene-9-carboxylic Acid (2) *n*-Butyllithium (1.1 N, 20 ml) was added to a suspension of selenoxanthene (**1**)[1] (4.9 g) in dry ether (150 ml). The reaction mixture was stirred for 30 min at room temperature and poured onto crushed dry ice. The aqueous mixture was made basic with 10% sodium hydroxide and extracted with dichloromethane. The extracts were dried ($MgSO_4$) and concentrated to dryness. Selenoxanthene (**1**) (0.56 g, 11.5%) was recovered. The aqueous layer was acidified with 10% hydrochloric acid and extracted with dichloromethane. The extracts were dried ($MgSO_4$) and concentrated to dryness to give a crystalline solid. Recrystallization from acetone–hexane afforded selenoxanthene-9-carboxylic acid (**2**) as colorless prisms (4.3 g, 74.6%), mp 237—239 °C. IR ν_{max}^{KBr} cm^{-1}: 3200—2400 (OH), 1695 (CO). MS *m/z*: 290 (M^+, Se=80). NMR (270 MHz) ($CDCl_3$) δ: 5.07 (1H, s, H-9), 7.17—7.33 (4H, m, ArH), 7.42 (2H, dd, J=7.48, 1.71 Hz, ArH), 7.58 (2H, dd, J=7.26, 1.28 Hz, ArH). *Anal.* Calcd for $C_{14}H_{10}O_2Se$: C, 58.15; H, 3.49. Found: C, 58.04; H, 3.44.

Ethyl Selenoxanthene-9-carboxylate (3) A mixture of **2** (2.0 g), concentrated sulfuric acid (3 drops) and ethanol (50 ml) was refluxed for 24 h. The cooled mixture was poured into water and extracted with dichloromethane. The extracts were washed with 5% sodium hydrogen carbonate, dried ($MgSO_4$) and concentrated to dryness. The crystalline solid was recrystallized from hexane to give colorless columns (2.0 g, 90.8%), mp 106.5 —107 °C. IR ν_{max}^{KBr} cm^{-1}: 1725 (CO). MS *m/z*: 318 (M^+, Se=80). NMR ($CDCl_3$) δ: 1.08 (3H, t, J=7.2 Hz, CH_3), 4.06 (2H, q, J=7.2 Hz, CH_2), 5.01 (1H, s, H-9), 7.03—7.78 (8H, m, ArH). *Anal.* Calcd for $C_{16}H_{14}O_2Se$: C, 60.58; H, 4.45. Found: C, 60.32; H, 4.48.

9-(Hydroxymethyl)selenoxanthene (4) A solution of **3** (2.0 g) in dry ether (30 ml) was added to a suspension of LAH (0.5 g) in dry ether (3 ml) under ice-cooling. The mixture was refluxed for 3 h and then cooled. Ethyl acetate was added to decompose excess LAH and aqueous ammonium chloride solution was added. The resulting mixture was extracted with ether. The extracts were dried ($MgSO_4$) and concentrated to dryness to leave a crystalline solid. Recrystallization from hexane gave colorless needles (1.6 g, 92.2%), mp 108 °C. IR ν_{max}^{KBr} cm^{-1}: 3220 (OH). MS *m/z*: 276 (M^+, Se=80). NMR (270 MHz) ($CDCl_3$) δ: 1.33 (1H, br t, OH), 3.82 (2H, m, CH_2), 4.26 (1H, t, J=6.0 Hz, H-9), 7.15—7.6 (8H, m, ArH). *Anal.* Calcd for $C_{14}H_{12}OSe$: C, 61.10; H, 4.40. Found: C, 61.21; H, 4.43.

9-Methylselenoxanthene (6) (a) Selenoxanthylium perchlorate (**5**)[1] (9.8 g) was added to an ethereal solution of methylmagnesium iodide [prepared from magnesium (3.5 g) and iodomethane (20.2 g) in dry ether (100 ml)]. After being refluxed for 30 min, the reaction mixture was cooled and decomposed with aqueous ammonium chloride and then with dilute hydrochloric acid. The white precipitate was collected, washed with ether and dried. A part of this sample was recrystallized from toluene to give colorless needles (0.8 g, 11.4%), mp >300 °C, which were identical with an authentic sample of 9,9′-biselenoxanthenyl (**7**).[9] The filtrate was extracted with ether. The extracts were dried ($MgSO_4$) and concentrated to dryness. The residue was recrystallized from ethanol to give colorless prisms of 9-

methylselenoxanthene (3.85 g, 52.1%), mp 94—95 °C. MS *m/z*: 260 (M^+, Se=80). NMR ($CDCl_3$) δ: 1.54 (3H, d, J=7.2 Hz, CH_3), 3.94 (1H, q, J=7.2 Hz, CH), 6.90—7.70 (8H, m, ArH). *Anal.* Calcd for $C_{14}H_{12}Se$: C, 64.87; H, 4.67. Found: C, 65.06; H, 4.53.

(b) A solution of *n*-butyllithium (1.6 N, 12.5 ml) in hexane was added to a suspension of selenoxanthene (**1**) (4.9 g) in dry ether (150 ml) under a nitrogen atmosphere at room temperature and the mixture was stirred for 30 min. Iodomethane (2.8 g) was gradually added to it. After the reaction had been continued for 2 h, the mixture was decomposed with aqueous ammonium chloride solution. The organic layer was separated and the aqueous layer was extracted with ether. The organic layer and the extracts were combined and dried ($MgSO_4$). The solvent was evaporated off and the residual solid was recrystallized from ethanol to give colorless prisms (5.1 g, 98.5%). This sample was identical with the specimen prepared by method (a). A small amount of 9,9-biselenoxanthenyl was obtained as insoluble crystals.

General Procedure for the Preparation of 9-(2-Hydroxyethyl)-selenoxanthenes (9—11) An ethereal solution of *n*-butyllithium (1.1 N) (10 ml) was gradually added to an ice-cold solution of a selenoxanthene (**1**, **6**, **8**) in dry tetrahydrofuran (THF) (50 ml). The reaction mixture was stirred for 1.5 h at room temperature. An ethereal solution of ethylene oxide (440 mg) was added to the reaction mixture at room temperature. The red color faded in a few minutes. After being stirred for 15 min, the mixture was decomposed with aqueous ammonium chloride solution. The organic layer was separated and the aqueous layer was extracted with ether. The organic layer and the extracts were combined, washed with water, dried ($MgSO_4$) and concentrated to dryness. The residue was separated by column chromatography on silica gel. The starting selenoxanthene (**1**, **6**, **8**) was recovered from the hexane–ethyl acetate (10:1) fractions and the title compound was obtained from the hexane–ethyl acetate (1:1) fractions. 9-(2-Hydroxyethyl)selenoxanthene (**9**) was obtained in 85.3% yield and selenoxanthene (**1**) was recovered in 13.7% yield. Compound **9** was recrystallized from dichloromethane–hexane to give colorless columns, mp 74—75 °C. IR ν_{max}^{KBr} cm^{-1}: 3250 (OH). MS *m/z*: 290 (M^+, Se=80). NMR ($CDCl_3$) δ: 1.52 (1H, br s, OH), 2.02 (2H, dt, J=7.8, 6.0 Hz, $\underline{CH_2}CH_2OH$), 3.45 (2H, t, J=6.0 Hz, CH_2OH), 4.30 (1H, t, J=7.8 Hz, H-9), 7.05—7.70 (8H, m, ArH). *Anal.* Calcd for $C_{15}H_{14}OSe$: C, 62.29; H, 4.88. Found: C, 62.30; H, 4.82. 9-(2-Hydroxyethyl)-9-methylselenoxanthene (**10**) was obtained in 62.3% yield and 9-methylselenoxanthene (**6**) was recovered in 6.0% yield. Compound **10** was recrystallized from dichloromethane–hexane to give colorless needles, mp 80—81 °C. IR ν_{max}^{KBr} cm^{-1}: 3170 (OH). MS *m/z*: 304 (M^+, Se=80). NMR ($CDCl_3$) δ: 1.35 (1H, br s, OH), 1.95 (3H, s, CH_3), 2.15 (2H, t, J=7.0 Hz, $\underline{CH_2}CH_2OH$), 3.20 (2H, t, J=7.0 Hz, CH_2OH), 6.90—7.70 (8H, m, ArH). *Anal.* Calcd for $C_{16}H_{16}OSe$: C, 63.37; H, 5.32. Found: C, 63.44; H, 5.24. 9-(2-Hydroxyethyl)-9-phenylselenoxanthene (**11**) was obtained in 63.8% yield and 9-phenylselenoxanthene (**8**) was recovered in 30.1% yield. Compound **11** was a viscous oil. IR ν_{max}^{film} cm^{-1}: 3350 (OH). High-resolution MS *m/z*: 366.0510 (M^+) Calcd for $C_{21}H_{18}OSe$ 366.0511. NMR ($CDCl_3$) δ: 1.47 (1H, br s, OH), 2.70 (2H, t, J=7.0 Hz, $\underline{CH_2}CH_2OH$), 3.57 (2H, J=7.0 Hz, CH_2OH), 6.75—7.65 (13H, m, ArH).

10-Chloro-10,9-epoxymethanoselenoxanthene (12) A solution of NCS (302 mg) in dry dichloromethane (20 ml) was added to a solution of **4** (622 mg) in dichloromethane (10 ml). After being stirred for 30 min at room temperature the reaction mixture was concentrated under reduced pressure. Ether was added to the concentrate and the crystals that precipitated were filtered off. Recrystallization from dichloromethane–ether gave colorless columns (584 mg, 83.5%), mp 112—113 °C (dec.). NMR ($CDCl_3$) δ: 3.93 (2H, d, J=1.8 Hz, CH_2), 4.66 (1H, t, J=1.8 Hz, H-9), 7.30—7.65 (6H, m, ArH), 8.23—8.53 (2H, m, H-4,5). *Anal.* Calcd for $C_{14}H_{11}ClOSe$: C, 54.30; H, 3.58. Found: C, 54.37; H, 3.72.

10-Chloro-10,9-epoxyethanoselenoxanthenes (14—16) Equimolar NCS in dry dichloromethane was added to a solution of a selenoxanthene (**9**—**11**) in dichloromethane in the same way as described for **12**. 10-Chloro-10,9-epoxyethanoselenoxanthene (**14**), colorless prisms (83.2%) from acetone, mp 137—139.5 °C (dec.). FD MS *m/z*: 324 (M^+). NMR (200 MHz) ($CDCl_3$) δ: 2.03—2.20 (2H, m, $\underline{CH_2}CH_2O$), 3.80—3.95 (2H, m, CH_2O), 4.54 (1H, t, J=4.5 Hz, H-9), 7.45—7.75 (6H, m, ArH), 8.27—8.43 (2H, m, H-4,5). *Anal.* Calcd for $C_{15}H_{13}ClOSe$: C, 55.66; H, 4.05. Found: C, 55.55; H, 3.89. 10-Chloro-10,9-epoxyethano-9-methylselenoxanthene (**15**), colorless prisms (81.2%) from acetone, mp 191—192 °C (dec.). MS *m/z*: 338 (M^+). NMR (200 MHz) ($CDCl_3$) δ: 1.85—2.00 (2H, m, $\underline{CH_2}CH_2O$), 2.07 (3H, s, CH_3), 3.84—4.00 (2H, m, CH_2O), 7.45—7.85 (6H, m, ArH), 8.37 (2H, dd, J=7.3, 1.7 Hz, H-4,5). *Anal.* Calcd for $C_{16}H_{15}ClOSe$: C, 56.91; H, 4.48. Found: C, 57.03; H, 4.43. 10-Chloro-10,9-epoxyethano-9-phenylselenoxanthene (**16**), colorless prisms (87.5%) from dichloromethane–ether, mp 182.5—183.5 °C (dec.). MS *m/z*: 400 (M^+, Se=80). NMR (200 MHz) ($CDCl_3$) δ: 2.40—2.60 (2H, m, $\underline{CH_2}CH_2O$), 3.72—3.93 (2H, m, CH_2O), 6.73—6.95 (2H, m, H-1,8), 6.95—7.25 (1H, m, H-2 of Ph), 7.30—7.85 (8H, m, ArH), 8.34 (2H, dd, J=7.1, 1.0 Hz, H-4,5). *Anal.* Calcd for $C_{21}H_{17}ClOSe$: C, 63.09; H, 4.29. Found: C, 63.12; H, 4.32.

10-Bromo-10,9-epoxyethanoselenoxanthene (17) A solution of NBS (615 mg) in dry dichloromethane (40 ml) was added to a solution of **9** (1.00 g) in dry dichloromethane (20 ml) at room temperature. The mixture was stirred for 30 min and then concentrated to half volume under reduced pressure. Ether was added to the concentrate. The crystals precipitated were collected and recrystallized from dichloromethane–ether to give yellow prisms (1.13 g, 88.9%), mp 115.5—117 °C (dec.). MS *m/z*: 368 (M^+, Se=80). NMR ($CDCl_3$) δ: 2.05—2.20 (2H, m, $\underline{CH_2}CH_2O$), 3.80—3.95 (2H, m, CH_2O), 4.54 (1H, t, J=4.0 Hz, H-9), 7.40—7.70 (6H, m, ArH), 8.43 (2H, d, J=7.1 Hz, H-4,5). *Anal.* Calcd for $C_{15}H_{13}BrOSe$: C, 48.94; H, 3.56. Found: C, 49.06; H, 3.50.

Reaction of the Selenurane 12 with Silver Perchlorate Silver perchlorate (150 mg) was added to a solution of **12** (200 mg) in 1,2-dichloroethane (20 ml). After the mixture had been stirred for 6 h, silver chloride was removed and the filtrate was concentrated to dryness under reduced pressure. Ether was added to the purple residue and the precipitate was filtered off. The purple crystals (213 mg, 96.2%) were identical with an authentic sample of selenoxanthylium perchlorate (**5**).[1)]

General Procedure for the Preparation of 10,9-Epoxyethanoselenoxanthenium Perchlorates (18—20) Equimolar silver perchlorate was added to a solution of a selenurane (**14**—**16**) in dry 1,2-dichloroethane (20 ml) at room temperature. The mixture was stirred for 1.5 h. Silver chloride was filtered off and washed with dichloromethane. The filtrate and washings were combined and concentrated to dryness. The residue was recrystallized from acetonitrile–ether. 10,9-Epoxyethanoselenoxanthenium perchlorate (**18**) (94.7%), colorless prisms, mp 163—165 °C (dec.). IR ν_{max}^{KBr} cm^{-1} 1100 (ClO_4^-). NMR (200 MHz) ($CDCl_3$) δ: 2.25—2.42 (2H, m, $\underline{CH_2}CH_2O$), 4.13—4.27 (2H, m, CH_2O), 4.52 (1H, t, J=4.5 Hz, H-9), 7.45—7.75 (6H, m, ArH), 8.37—8.47 (2H, m, H-4,5). (CF_3CO_2H) δ: 2.40—2.65 (2H, m, $\underline{CH_2}CH_2O$), 4.28—4.53 (2H, m, CH_2O), 4.67 (1H, t, J=4.5 Hz, H-9), 7.50—8.00 (6H, m, ArH), 8.10—8.33 (2H, m, H-4,5). *Anal.* Calcd for $C_{15}H_{13}ClO_5Se$: C, 46.47; H, 3.38. Found: C, 46.46; H, 3.32. 10,9-Epoxyethano-9-methylselenoxanthenium perchlorate (**19**) (61.6%), colorless prisms, mp 224—226 °C (dec.). IR ν_{max}^{KBr} cm^{-1}: 1100 (ClO_4^-). NMR (200 MHz) ($CDCl_3$) δ: 2.07 (3H, s, CH_3), 2.13—2.30 (2H, m, $\underline{CH_2}CH_2O$), 4.18—4.30 (2H, m, CH_2O), 7.55—7.85 (6H, m, ArH), 8.44 (2H, dd, J=7.0, 1.5 Hz, H-4,5); (CF_3CO_2H) δ: 2.16 (3H, s, CH_3), 2.20—2.47 (2H, m, $\underline{CH_2}CH_2O$), 4.32—4.58 (2H, m, CH_2O), 7.52—8.12 (6H, m, ArH), 8.22 (2H, dd, J=7.0, 1.5 Hz, H-4,5). *Anal.* Calcd for $C_{16}H_{15}ClO_5Se$: C, 47.84; H, 3.76. Found: C, 47.71; H, 3.78. 10,9-Epoxyethano-9-phenylselenoxanthenium perchlorate (**20**) (96.8%), colorless needles from acetonitrile–ether, mp 213.5—215.5 °C (dec.). IR ν_{max}^{KBr} cm^{-1}: 1100 (ClO_4^-). NMR ($CDCl_3$) (200 MHz) δ: 2.60—2.73 (2H, m, $\underline{CH_2}CH_2O$), 4.05—4.18 (2H, m, CH_2O), 6.91 (2H, dd, J=7.9, 1.7 Hz, H-1,8), 6.9—7.05 (1H, m, ArH), 7.36—7.70 (8H, m, ArH), 8.46 (2H, dd, J=7.3, 1.7 Hz, H-4,5); (CF_3CO_2H) δ: 2.74—3.00 (2H, m, $\underline{CH_2}CH_2O$), 4.22—4.50 (2H, m, CH_2O), 6.90—7.35 (3H, m, H-1,8, ArH), 7.4—7.93 (8H, m, ArH), 8.16—8.40 (2H, m, H-4,5). *Anal.* Calcd for $C_{21}H_{17}ClO_5Se$: C, 54.39; H, 3.69. Found: C, 54.15; H, 3.70.

9-Phenylselenoxanthene-9-carboxylic Acid (21) *n*-Butyllithium (1.1 N) (20 ml) was added to a solution of 9-phenylselenoxanthene (**8**)[2)] (6.42 g) in dry THF (100 ml) with stirring at 0 °C. After being stirred for 30 min at room temperature, the reaction mixture was poured onto crushed dry ice and water was added to it. The mixture was made basic with 10% sodium hydroxide and then extracted with dichloromethane. The extracts were dried ($MgSO_4$) and concentrated to dryness to give **8** (1.14 g, 17.7%). The aqueous layer was treated with 10% hydrochloric acid and extracted with dichloromethane. The extracts were dried ($MgSO_4$) and concentrated to dryness. The residual solid was recrystallized from acetone–hexane to give colorless needles (5.98 g, 81.9%), mp 177—178.5 °C (dec.). IR ν_{max}^{KBr} cm^{-1}: 3600—2400 (OH), 1690 (CO). NMR ($CDCl_3$) δ: 6.95—7.75 (13H, m, ArH), 8.55 (1H, br s, CO_2H). *Anal.* Calcd for $C_{20}H_{14}O_2Se$: C, 65.76; H, 3.86. Found: C, 65.95; H, 4.06.

Reaction of 21 with NCS A solution of NCS (73 mg) in dry dichloromethane (10 ml) was added to a solution of **21** (200 mg) in dry dichloromethane (20 ml) at room temperature. The reaction mixture turned purple immediately. The reaction was continued for 2 h and quenched with 10 drops of 28% sodium methoxide in methanol. The reaction mixture

was poured into water and extracted with dichloromethane. The extracts were dried and concentrated to dryness. The residual solid was separated by preparative TLC on silica gel using chloroform–hexane (1 : 1) to give 9-methoxy-9-phenylselenoxanthene (**25**)[9] (123 mg, 64.1%) and 9-phenylselenoxanthen-9-ol (**26**)[9] (35 mg, 18.9%).

10-Chloro-10,9-epoxy-9-phenylselenoxanthene (27) A solution of NCS (1.33 g, 10 mmol) in dry dichloromethane (50 ml) was added to a solution of 9-phenylselenoxanthen-9-ol (**26**)[9] (3.37 g, 10 mmol) in dry dichloromethane (30 ml). After being stirred for 48 h at room temperature, the reaction mixture was concentrated to dryness. The residue was triturated with ether and recrystallized from dichloromethane–ether to give colorless needles (2.69 g, 72.3%), mp 240—243 °C (dec.). NMR ($CDCl_3$) δ: 7.2—8.0 (11H, m, ArH), 8.30—8.60 (2H, m, H-4,5). MS *m/z*: 372 (Se=80, Cl=35). *Anal.* Calcd for $C_{19}H_{13}ClOSe$: C, 61.39; H, 3.53. Found: C, 61.44; H, 3.45.

2-(Phenylseleno)benzyl Alcohol (29) Sodium borohydride (2.3 g) was added to a stirred solution of 2-(phenylseleno)benzaldehyde (**28**)[2] (13.3 g) in ethanol (270 ml). After the reaction mixture had been stirred for 30 min, ethanol was evaporated off. The residual oil was poured into water and extracted with dichloromethane. The extracts were dried ($MgSO_4$) and evaporated under reduced pressure. A yellow oil obtained quantitatively was used without further purification. High-resolution MS *m/z*: 264.0067 (M^+) Calcd for $C_{13}H_{12}OSe$ 264.0053. IR ν_{max}^{film} cm^{-1}: 3600—3100 (OH), NMR ($CDCl_3$) δ: 2.38 (1H, t, J=6.0 Hz, OH), 4.78 (2H, d, J=6.0 Hz, $PhCH_2$), 7.1—9.6 (9H, m, ArH).

Mesityl[*o*-(phenylseleno)phenyl]methanol (31) An ethereal solution of **28** (7.43 g) was added to an ethereal solution of mesitylmagnesium bromide [prepared from 1-bromomesitylene (17 g) and magnesium (2.08 g) in dry ether (50 ml)] with stirring at ice-bath temperature. The reaction mixture was warmed to room temperature, and refluxed for 3 h. An aqueous ammonium chloride solution was added to the cooled reaction mixture. The organic layer was separated, washed with water, dried ($MgSO_4$) and concentrated to dryness. The residue was chromatographed on silica gel using benzene–hexane (1 : 1) and recrystallized from hexane to give colorless prisms (7.6 g, 70.7%), mp 95—96 °C. MS *m/z*: 382 (Se=80). IR ν_{max}^{KBr} cm^{-1}: 3530 (OH). NMR ($CDCl_3$) δ: 2.19 (6H, s, $CH_3\times2$), 2.26 (3H, s, CH_3), 2.56 (1H, d, J=4.5 Hz, OH), 6.36 (1H, d, J=4.5 Hz, CH), 6.84 (2H, s, ArH), 6.95—7.6 (9H, m, ArH). *Anal.* Calcd for $C_{22}H_{22}OSe$: C, 69.29; H, 5.81. Found: C, 69.24; H, 5.69.

1-Chloro-1-phenyl-3*H*-2,1-benzoxaselenoles (32—34) A solution of NCS (1.0 g, 7.65 mmol) in dry dichloromethane (40 ml) was added to a solution of a benzyl alcohol (**29—31**) (7.65 mmol) in dry dichloromethane (20 ml) at room temperature. The mixture was stirred for 30 min and then the solvent was evaporated. Ether was added to the residue. The precipitate was filtered, washed twice with ether and recrystallized from dichloromethane–ether. 1-Chloro-1-phenyl-3*H*-2,1-benzoxaselenole (**32**), colorless columns (67.8%), mp 149.5—151 °C (dec.). NMR ($CDCl_3$) δ: 4.99 (1H, d, J=13.8 Hz, CH_2), 5.46 (1H, d, J=13.8 Hz, CH_2), 7.25—7.9 (8H, m, ArH), 8.80—9.15 (1H, m, H-7). *Anal.* Calcd for $C_{13}H_{11}ClOSe$: C, 52.46; H, 3.73. Found: C, 52.48; H, 3.74. 1-Chloro-1,3-diphenyl-3*H*-2,1-benzoxaselenole (**33**), colorless columns (86.8%), mp 159—160 °C (dec.). NMR ($CDCl_3$) δ: 5.85 (1H, s, CH), 6.0—7.9 (13H, m, ArH), 8.95—9.20 (1H, m, H-7). *Anal.* Calcd for $C_{19}H_{15}ClOSe$: C, 61.06; H, 4.05. Found: C, 60.78; H, 3.99. 1-Chloro-3-mesityl-1-phenyl-3*H*-2,1-benzoxaselenole (**34**), colorless prisms (84.0%), mp 191—192 °C (dec.). NMR ($CDCl_3$) δ: 1.85 (3H, br s, CH_3), 2.13 (3H, br s, CH_3), 2.25 (3H, s, CH_3), 6.20 (1H, br s, CH), 6.75—7.0 (2H, br s, ArH), 7.38—7.88 (8H, m, ArH), 8.95—9.15 (1H, m, H-7). *Anal.* Calcd for $C_{22}H_{21}ClOSe$: C, 63.55; H, 5.09. Found: C, 63.30; H, 4.98.

1-Phenyl-3*H*-2,1-benzoxaselenolium Perchlorate (35) Silver perchlorate (38.7 mg) was added to a solution of **32** (50 mg) in dry dichloromethane (10 ml) with stirring at room temperature and the mixture was stirred for 2 h. The precipitate was filtered off and washed with acetonitrile. The filtrate and the washings were combined and concentrated to dryness under reduced pressure. The residual solid was washed with ether and recrystallized from acetonitrile–ether to give colorless prisms (50.5 mg, 83.2%), mp 196—197.5 °C (dec.). IR ν_{max}^{KBr} cm^{-1}: 1100 (ClO_4^-). NMR (CF_3CO_2H) δ: 5.85 (2H, br s, CH_2), 7.5—8.1 (8H, m, ArH), 8.1—8.3 (1H, m, H-7). *Anal.* Calcd for $C_{13}H_{11}ClO_5Se$: C, 43.18, 3.07. Found: C, 43.23; H, 3.03.

Reaction of 10-Chloro-10,9-epoxy-9-phenylselenoxanthene (27) with Sodium Acetylacetonide Sodium hydride (60% pure in mineral oil) (82.3 mg) was added to an ice-cold solution of acetylacetone (103 mg) in THF (20 ml). The reaction mixture was stirred for 1 h at room temperature. The selenurane **27** (382 mg) was added to the solution of sodium acetylacetonide with stirring at room temperature and the mixture was stirred for 30 min and then poured into water. The product was extracted with dichloromethane. The extracts were dried ($MgSO_4$) and concentrated to dryness. The residual solid was recrystallized from dichloromethane–ether to give (9-hydroxyselenoxanten-10-io)diacetylmethanide (**36**), colorless prisms (332 mg, 74.2%), mp 201—203 °C. IR ν_{max}^{KBr} cm^{-1}: 3280 (OH), 1560 (CO). MS *m/z*: 436 (M^+, Se=80). NMR (270 MHz) ($CDCl_3$) δ: 2.21 (6H, s, CH_3), 7.10—7.22 (2H, m, H-1,8), 7.22—7.35 (3H, m, H-3,4,5 of Ph), 7.45—7.70 (8H, m, ArH). *Anal.* Calcd for $C_{24}H_{20}O_3Se$: C, 66.21; H, 4.63. Found: C, 65.96; H, 4.54.

Reaction of 10-Chloro-10,9-epoxyethano-9-phenylselenoxanthene (16) with Sodium Acetylacetonide A solution of sodium acetylacetonide in THF was prepared by adding sodium hydride (60% pure in mineral oil) (40.7 mg) to a solution of acetylacetone (102 mg) in dry THF (20 ml). The selenurane (**16**) (407 mg) was added to the solution of sodium acetylacetonide with stirring at room temperature. The mixture was stirred for 10 min and water was added to it. The resulting mixture was extracted with dichloromethane. The extracts were washed with water, dried ($MgSO_4$) and concentrated to dryness. The residue was chromatographed on silica gel using acetone to give [9-(2-hydroxyethyl)-9-phenylselenoxanthen-10-io]diacetylmethanide (**37**). Recrystallization of the ylide (**37**) from dichloromethane–hexane gave colorless needles (334 mg, 70.8%), mp 209—211 °C (dec.). IR ν_{max}^{KBr} cm^{-1}: 3300 (OH), 1600—1520 (CO). MS *m/z*: 464 (M^+, Se=80). NMR (200 MHz) ($CDCl_3$) δ: 2.46 (6H, s, $CH_3\times2$), 2.69 (2H, t, J=7.1 Hz, $\underline{CH_2}CH_2OH$), 3.44 (2H, m, CH_2OH), 6.86—6.91 (2H, m, ArH), 7.20—7.42 (9H, m, ArH), 7.42—7.57 (2H, m, ArH).
Anal. Calcd for $C_{26}H_{24}O_3Se$: C, 67.39; H, 5.22. Found: C, 67.20; H, 5.29.

Hydrolysis of 14 (a) With Sodium Hydroxide: A mixture of a solution of **14** (200 mg) in dichloromethane (50 ml) and 10% aqueous sodium hydroxide (10 ml) was shaken in a separatory funnel for 2 min. The organic layer was separated, dried ($MgSO_4$) and concentrated to dryness under reduced pressure. The product (177 mg, 93.8%) was identical with an authentic sample of 9-(2-hydroxyethyl)selenoxanthene 10-oxide (**38**).

(b) With Silver Acetate: Silver acetate (155 mg) was added to a solution of **14** (300 mg) in 1,2-dichloroethane (20 ml) and the mixture was stirred for 1 h at room temperature. The precipitate was filtered off and washed with dichloromethane. The filtrate and the washings were combined and concentrated to dryness. Ether was added to the residue and the crystals were collected. The product (105 mg, 37.1%) was identical with the selenoxide **38**.

Hydrolysis of 16 (a) With Sodium Hydroxide: A mixture of a solution of **16** (300 mg) in dichloromethane (50 ml) and 10% aqueous sodium hydroxide (10 ml) was shaken in a separatory funnel for 2 min. The organic layer was separated, dried ($MgSO_4$) and concentrated to dryness under reduced pressure. The product (271 mg, 94.7%) was identical with an authentic sample of 9-(2-hydroxyethyl)-9-phenylselenoxanthene 10-oxide (**39**). IR ν_{max}^{KBr} cm^{-1}: 3200 (OH), 820 (Se→O). NMR (200 MHz) ($CDCl_3$) δ: 2.48 (t, J=7.1 Hz), 2.96 (t, J=6.6 Hz, $\underline{CH_2}CH_2O$), 3.44 (t, J=7.1 Hz), 3.66 (t, J=6.6 Hz, CH_2O), 6.81 (2H, dd, J=8.1, 1.0 Hz, H-1,8), 7.20—7.70 (9H, m, ArH), 7.95, 8.10 (2H, J=7.6, 1.5 Hz, ArH). The selenoxide **39** was a mixture of stereoisomers and the isomer ratio (Z/E=6/5) was determined from the intensities of the triplets due to the 1′-methylene $\underline{CH_2}CH_2O$ groups.

(b) By TLC: The selenurane **16** was subjected to preparative TLC on silica gel using ethyl acetate–methanol (4 : 1). The product was quantitatively obtained and was identical with the authentic selenoxide **39**.

***E*-9-(2-Hydroxyethyl)selenoxanthene 10-Oxide (38)** *m*-CPBA (85% pure) (0.77 g) was added to a solution of **9** (1.00 g) in dichloromethane (100 ml) with stirring under ice-cooling. The mixture was stirred for 10 min at that temperature and then poured into water. The organic layer was separated and the aqueous layer was extracted with dichloromethane. The organic layer and the extracts were combined, washed with an aqueous sodium hydrogen carbonate solution and then water, and dried ($MgSO_4$). The solvent was removed under reduced pressure to give colorless prisms (0.84 g, 79.7%), mp 212.5—214 °C (dec.). IR ν_{max}^{KBr} cm^{-1}: 3280 (OH), 820 (Se→O). NMR (200 MHz) ($CDCl_3$) δ: 1.84 (2H, dt, J=7.8, 5.9 Hz, $\underline{CH_2}CH_2O$), 3.57 (2H, m, CH_2O), 4.51 (1H, t, J=7.8 Hz, H-9), 7.44—7.54 (6H, m, ArH), 8.02—8.10 (2H, m, H-4,5). *Anal.* Calcd for $C_{15}H_{14}O_2Se$: C, 59.02; H, 4.62. Found: C, 58.88; H, 4.48.

9-(2-Hydroxyethyl)-9-phenylselenoxanthene 10-Oxide (39) The selenoxanthene **11** was oxidized with *m*-CPBA in the same way as described for **9**. The selenoxide **39** was obtained in 90.5% yield as colorless columns (from dichloromethane–ether), mp 192—194 °C IR ν_{max}^{KBr} cm^{-1}: 3200 (OH), 820 (Se→O). NMR (200 MHz) ($CDCl_3$) δ: 2.48 (t, J=7.1 Hz, $\underline{CH_2}CH_2O$), 3.44 (t, J=7.1 Hz, CH_2OH), 8.10 (dd, J=7.6, 1.5 Hz, ArH) for *Z*-isomer and 2.96 (t, J=6.6 Hz, $\underline{CH_2}CH_2O$), 3.66 (t, J=6.6 Hz, CH_2OH), 7.95

(dd, J=7.6, 1.5 Hz, ArH) for *E*-isomer, 6.81 (2H, dd, J=8.1, 1.0 Hz, H-1,8), 7.20—7.70 (9H, m, ArH). The selenoxide **39** was a mixture of stereoisomers in the ratio of Z/E=6/5. *Anal.* Calcd for $C_{15}H_{14}O_2Se$: C, 59.02; H, 4.62. Found: C, 58.88; H, 4.48.

Reduction of 14 with Sodium Borohydride Sodium borohydride (58 mg) was added to a solution of **14** (100 mg) in a mixture of ethanol (10 ml) and dichloromethane (10 ml), with stirring at room temperature. The mixture was stirred for 10 min and then the solvent was removed. Water was added to the residue and the mixture was extracted with dichloromethane. The extracts were washed with water, dried ($MgSO_4$) and concentrated to dryness. The residue was recrystallized from dichloromethane–ether to give 9-(2-hydroxyethyl)selenoxanthene (**9**) (87.0 mg, 97.4%).

Reaction of 14 with Hydrogen Chloride A saturated solution with hydrogen chloride in ether (10 ml) was added to a solution of **14** (200 mg) in dry dichloromethane (10 ml) and the mixture was stirred for 30 min at room temperature. The solvent was removed under reduced pressure. The residue was recrystallized from acetonitrile–ether to give 9-(2-hydroxyethyl)selenoxanthene dichloride (**40**) (200 mg, 89.9%) as pale yellow prisms, mp 130—131.5 °C. IR ν_{max}^{KBr} cm^{-1}: 3510 (OH). *Anal.* Calcd for $C_{15}H_{14}Cl_2OSe$: Cm 50.03; H, 3.92. Found: C, 49.80; H, 3.86.

Thermal Reactions of 14 (a) The selenurane **14** (500 mg) was heated at 150 °C for 10 min and the products were separated by preparative TLC on silica gel using benzene–ethyl acetate (20:1). 9-(1-Chloro-2-hydroxyethylidene)selenoxanthene (**41**) was recrystallized from benzene–hexane to give colorless columns (138 mg, 27.6%), mp 161.5—162.5 °C. IR ν_{max}^{KBr} cm^{-1}: 3130 (OH). NMR (200 MHz) ($CDCl_3$) δ: 2.23 (1H, dd, J=5.1, 7.2 Hz, OH), 4.36 (1H, dd, J=5.1, 12.7 Hz, CH_2), 4.50 (1H, dd, J=7.2, 12.7 Hz, CH_2), 7.15—7.40 (4H, m, ArH), 7.51 (1H, dd, J=1.5, 8.8 Hz, ArH), 7.62 (2H, dd, J=1.7, 6.7 Hz, ArH), 7.77 (1H, dd, J=1.5, 9.3 Hz, ArH). ^{13}C-NMR ($CDCl_3$) δ: 64.68 (t, CH_2), 126.25, 126.81, 127.51, 127.71, 128.80, 129.43, 129.68, 130.09, 130.92, 131.75, 132.82, 135.69, 135.78, 137.85 (C-9, C-1′ and ArC). *Anal.* Calcd for $C_{15}H_{11}ClOSe$: C, 56.01; H, 3.45. Found: C, 56.17; H, 3.39. 9-(2-Hydroxyethyl)selenoxanthene (**9**) (152 mg, 30.4%) was identical with an authentic sample.

(b) A solution of the selenurane **14** (300 mg) in dry ethanol (30 ml) was refluxed for 3 h under a nitrogen atmosphere. The solvent was removed under reduced pressure and the residue was separated by preparative TLC on silica gel using benzene–ethyl acetate (20:1). 9-Ethoxy-9-(1-chloro-2-hydroxyethyl)selenoxanthene (**42**) was recrystallized from hexane to give colorless prisms (141 mg, 42.1%), mp 99—101 °C. MS m/z: 368 (M^+, Se=80, Cl=35). IR ν_{max}^{KBr} cm^{-1}: 3470 (OH). NMR (270 MHz) ($CDCl_3$) δ: 1.30 (3H, t, J=7.1 Hz, CH_3), 2.54 (1H, dd, J=8.8, 3.9 Hz, OH), 3.31 (2H, q, J=7.1 Hz, $CH_3\underline{CH_2}O$), 3.61 (1H, ddd, J=7.3, 8.8, 12.2 Hz, $CH\underline{CH_2}OH$), 3.80 (1H, ddd, J=3.9, 3.9, 12.2 Hz, $CH\underline{CH_2}OH$), 4.33 (1H, dd, J=7.3, 3.9 Hz, CHCl), 7.23—7.40 (4H, m, ArH), 7.46 (2H, dd, J=1.7, 7.6 Hz, ArH), 7.72—7.83 (2H, m, ArH). ^{13}C-NMR ($CDCl_3$) δ: 15.1 (q, CH_3), 59.7 (t, $CH_3\underline{CH_2}CH_2O$), 63.2 (t, CH_2OH), 70.8 (d, CH), 83.5 (s, C-9), 126.2, 126.3, 128.3, 130.0, 130.4, 132.9, 133.2 (ArC). *Anal.* Calcd for $C_{17}H_{17}ClO_2Se$: C, 55.53; H, 4.66. Found: C, 55.68; H, 4.67. 9-(2-Hydroxyethyl)selenoxanthene (**9**) (126 mg, 47.1%) was identical with an authentic sample.

Reduction of the Selenurane 32 with Sodium Borohydride Sodium borohydride (63 mg) was added to a solution of **32** (100 mg) in a mixture of ethanol (10 ml) and dichloromethane (10 ml) with stirring at room temperature. The reaction mixture was stirred for 10 min and the solvent was evaporated off. Water was added to the residue and the mixture was extracted with dichloromethane. The extracts were dried ($MgSO_4$) and concentrated to dryness. The residual oil (80 mg, 90.7%) was identical with 2-(phenylseleno)benzyl alcohol (**29**).

Hydrolysis of 32 with Sodium Hydroxide A solution of **32** (200 mg) in dichloromethane (10 ml) was shaken with 10% sodium hydroxide (2 ml) in a separatory funnel for 2 min. The organic layer was separated and the aqueous layer was extracted with dichloromethane. The organic layer and the extracts were combined, dried ($MgSO_4$) and concentrated to dryness. The residual solid was recrystallized from dichloromethane–hexane to give 1-hydroxy-1-phenyl-3*H*-2,1-benzoxaselenole (**43**) (180 mg, 96.1%), mp 149.5—151 °C. IR ν_{max}^{KBr} cm^{-1}: 3300—2200 (OH). NMR ($CDCl_3$) δ: 4.46 (1H, d, J=13.8 Hz, CH_2), 4.82 (1H, d, J=13.8 Hz, CH_2), 6.9—7.9 (8H, m, ArH), 7.95—8.30 (1H, m, H-7). *Anal.* Calcd for $C_{13}H_{12}O_2Se$: C, 55.93; H, 4.33. Found: C, 55.86; H, 4.32. The product **43** was identical with an authentic sample which was synthesized as described below.

1-Hydroxy-1-phenyl-3*H*-2,1-benzoxaselenole (43) *m*-CPBA (85% pure) (1.16 g) was gradually added to a solution of **29** (1.5 g) in dichloromethane (30 ml) under ice-cooling. The reaction mixture was stirred for 5 h at room temperature and poured into water. The organic layer was separated, washed with an aqueous sodium hydrogen carbonate solution, dried ($MgSO_4$) and concentrated to dryness. The residue was recrystallized from dichloromethane–ether as colorless prisms (1.2 g, 75.0%), mp 149.5—151 °C. IR ν_{max}^{KBr} cm^{-1}: 3400—3200 (OH). NMR ($CDCl_3$) δ: 4.46 (1H, d, J=13.8 Hz, CH_2), 4.82 (1H, d, J=13.8 Hz, CH_2), 6.9—7.9 (8H, m, ArH), 7.95—8.30 (1H, m, H-7). *Anal.* Calcd for $C_{13}H_{12}O_2Se$: C, 55.93; H, 4.33. Found: C, 55.91; H, 4.35.

Thermal Reaction of 32 The selenurane **32** (200 mg) was heated at 195—200 °C for 10 min under a nitrogen atmosphere. The products were separated by preparative TLC on silica gel using chloroform–hexane (1:3). 2-(Phenylseleno)benzy chloride (**45**) (45 mg, 23.8%) was obtained as a yellow oil. MS m/z: 282 (M^+, Se=80, Cl=35). NMR ($CDCl_3$) δ: 4.81 (2H, s, CH_2), 7.00—7.75 (9H, m, ArH). This product was identical with an authentic sample. 2-(Phenylseleno)benzyl 2-(phenylseleno)benzoate (**46**) was recrystallized from hexane to give pale yellow prisms (22 mg, 12.5%), mp 107.5—108.5 °C. MS m/z: 524 (M^+, Se=80). IR ν_{max}^{KBr} cm^{-1}: 1703 (CO). NMR ($CDCl_3$) δ: 5.57 (2H, s, CH_2), 6.8—7.85 (16H, m, ArH), 7.9—8.1 (1H, m, ArH). *Anal.* Calcd for $C_{26}H_{20}O_2Se_2$: C, 59.78; H, 3.86. Found: C, 60.03; H, 3.85. 2-(Phenylseleno)benzaldehyde (**28**) (38 mg, 21.8%) was obtained.

2-(Phenylseleno)benzyl Chloride (45) Thionyl chloride (5.5 g) was added dropwise to a mixture of the benzyl alcohol **29** (11.5 g) and pyridine (3.7 g) under ice-cooling. After being stirred for 1 d, the reaction mixture was warmed at 40 °C for 1 h, cooled to room temperature, poured into water, and extracted with benzene. The extracts were washed with dilute hydrochloric acid and then water, dried ($MgSO_4$) and concentrated to dryness, giving a yellow oil (11.5 g, 94.0%). High-resolution MS m/z: 281.9714 (M^+) Calcd for $C_{13}H_{11}ClSe$ 281.9719. NMR ($CDCl_3$) δ: 4.81 (2H, s, CH_2), 7.00—7.75 (9H, m, ArH).

Thermal Reaction of 33 The selenurane **33** (100 mg) was heated at 195—200 °C for 10 min under a nitrogen atmosphere. The product was separated by preparative TLC on silica gel using chloroform–hexane (1:1). 2-(Phenylseleno)benzophenone (**47**) was obtained as an oil (67 mg, 74.5%) and was identical with an authentic sample.[9]

Determination of the Crystal Structure of the Selenurane 14 The crystal data and intensity data of **14** were derived from measurements on a Syntex R3 four-circle diffractometer with graphite-monochromated MoK_α radiation. Crystal data; $C_{15}H_{13}ClOSe$, monoclinic, space group $C2/c$, a=18.752(13), b=9.975(7), c=14.966(10) Å; β=101.21(5), D_x=1.49 $g\cdot cm^{-3}$, Z=8 and μ (MoK_α)=31.1 cm^{-1}. A total of 1796 independent reflections was collected within 2θ less than 45°, among which 1354 reflections ($I>1.96\sigma(I)$) were used as observed. Lorentz and polarization corrections were applied, but no absorption corrections were made. The structure was solved by the direct method using MULTAN with a Syntex XTL program. The refinement of atomic parameters of the non-hydrogen atoms was carried out by block-diagonal least-squares calculations. The final R-value was 0.11 assuming anisotropic thermal motions for non-hydrogen atoms. The molecular structure of the selenurane **14** is illustrated in Fig. 1. The final atomic parameters are given in Table I. Bond distances and angles are listed in Table II.

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