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Selenabenzenes. II. Reaction Mechanism of 9-Phenylselenoxanthylium Salt with Organometallic Reagents.[1] On 10-Selenaänthracene and Selenoxanthene Derivatives

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The mechanism of the reactions between 9-phenylselenoxanthylium perchlorate (IIb) with phenyllithium or Grignard reagents was clarified by the studies of the eloctron spin resonancl spectroscopy and the chemical reactivities of 9-phenylselenoxanthyl radical (V), which was a reaction intermediate.

These experimental results show that the radical mechanism considerably contributes to the reactions between IIIb and organometallic reagents.

In our previous report, the preparation of novel aromatic heterocycles, so-called selenabenzenes which contain a decet selenium atom, such as 10-selenaänthracenes, has been performed by the reactions of selenoxanthylium salts with aryllithium.[1]

The authors closely examined the mechanism of the formation of 10-selenaänthracene or selenoxanthene derivatives (III or IV) by the reactions of 9-phenylselenoxanthylium perchlorate (IIb) with aryllithium and Grignard reagents. The results will be reported below.

Chart 1 shows the preparation of III and IV by a synthetic route similar to those of corresponding sulfur compounds, 10-thiaänthracene derivatives (I).[3] When IIb was allowed to react in the absence of oxygen with phenyllithium and various Grignard reagents in ether or with zinc or potassium in THF at room temperature, almost the same electron spin resonance (ESR) spectra with a hyperfine structure were observed as shown in Fig. 1. The intensity of the spectra showed that the concentration was as high as 3% immediately after the reaction and that the concentration then gradually decreased.

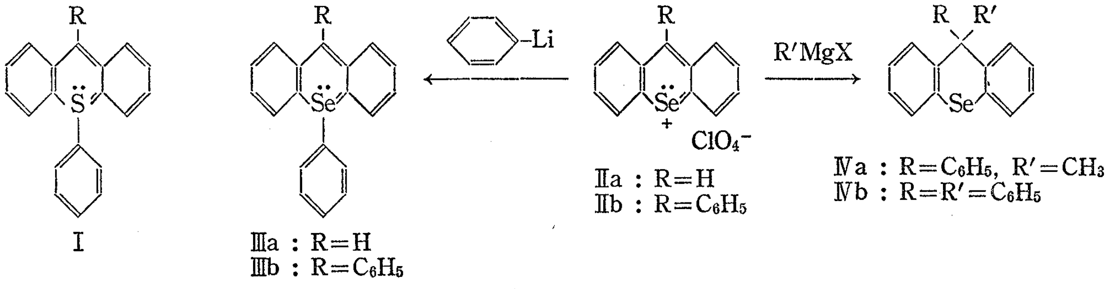

Chart 1

This spectrum suggests that the radical is possibly an intermediate of the reactions. Therefore, the authors now studied on the ESR spectra of the radical (V) as well as on the chemical reactivity of the radical (V) as a reaction intermediate. Thus, it has been found

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[1] Part I: M. Hori, T. Kataoka, and Chen-Fu Hsü, *Chem. Pharm. Bull.* (Tokyo), **22**, 15 (1974); A part of this work was presented at International Symposium on the Chemistry of Nonbenzenoid Aromatic Compounds, Sendai, August, 1970, Abstracts of Papers, p. 35; M. Hori, T. Kataoka, H. Shimizu, and C. Hsü, *Chem. Letts.*, **1973**, 391.

[2] Location: *a*) *492-36, Mitahora, Gifu*; *b*) *Juso-Nishino-cho, Higashiyodogawa-ku, Osaka.*

[3] C.C. Price, M. Hori, T. Parasaran, and M. Polk, *J. Am. Chem. Soc.*, **85**, 2278 (1963).

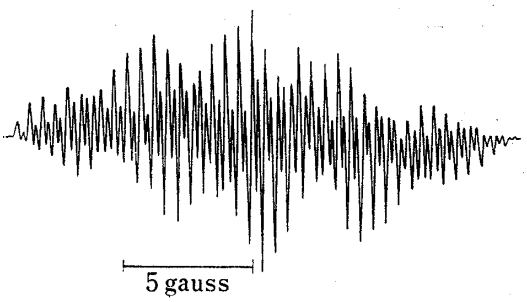

Fig. 1. ESR Spectrum of 9-Phenylselenoxanthyl Radical (V)

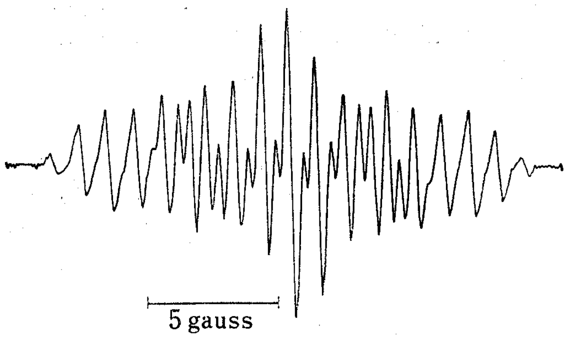

Fig. 2. ESR Spectrum of 9-Phenyl(-d_5)-selenoxanthyl Radical (X)

that a radical mechanism is related to the title reaction to a considerable degree besides the ionic mechanism[4] as following results show.

1. These ESR spectra were analyzed as follows on the assumption that radical (V) is formed as an intermediate: By the reaction of 9-phenyl(-d_5)selenoxanthylium salt (VIII) and zinc in THF or by the reaction of VIII and phenylmagnesium bromide in ether, the simple ESR spectrum of 9-phenyl(-d_5)selenoxanthyl radical (X) was obtained as shown in Fig. 2.

Chart 2 shows the synthesis of VIII. Thus, VIII was obtained by the reaction of 70% perchloric acid with VII, synthesized from selenoxanthone (VI) and phenyl(-d_5)magnesium bromide in ether. Reactions of VIII with $LiAlH_4$ and dilute NaOH gave IX and VII, respectively. These reaction products support the structure of VIII.

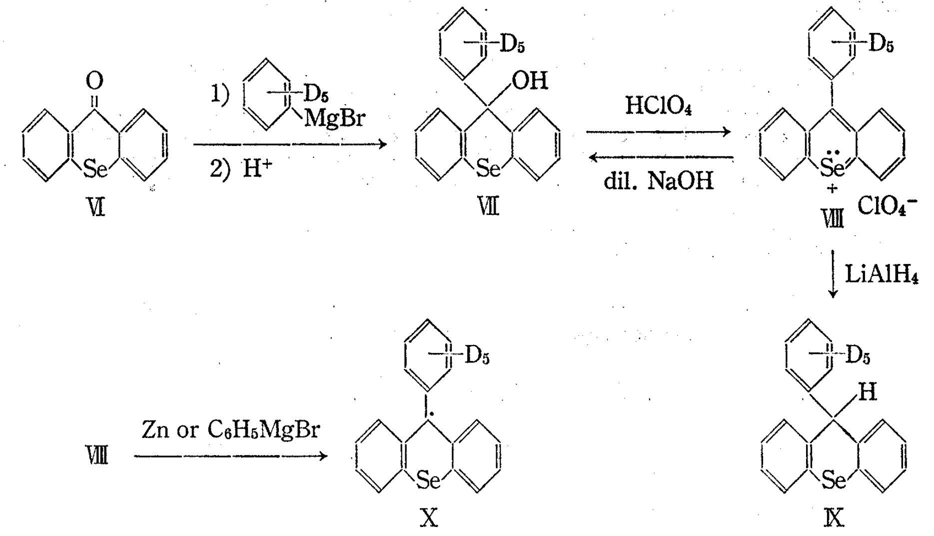

Chart 2

By the comparison with the results of analysis of X as shown in Table II, hyperfine splitting constants of V were estimated by the trial-and-error method from the odd electron densities ρ, which requires that $A_{iH} = -Q\rho_i$ in gauss. A_{iH} and ρ_i, were calculated by the McLachlan SCF-MO computation. The ESR spectra of radical (V) calculated from these values were close to experimental spectra. Therefore, radical (V) was identified as 9-phenylselenoxanthyl radical.

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[4] The title reaction might partially proceed by the ionic mechanism, in which IIa and IIb couple with a carbanion of the organometallic reagents, at the positive carbon or selenium atom to form III or IV. However, it is difficult to determine the extent of the contribution of the ionic mechanism.

The ESR spectrum of this radical (V) was very similar to that of the radical obtained by Maruyama, *et al.*[5] from 9-phenylselenoxanthyl chloride by the Gomberg method.[6]

Table I summarizes the results of analysis of the ESR spectrum of V obtained by two different methods.

TABLE I. Odd Electron Densities (ρ_i) by MO Calculation and Proton Hyperfine Splitting Constants ($\lvert A_{iH}\rvert=-27\rho_i$ in gauss) of 9-Phenylselenoxanthyl Radical (V)

	Reference			
Position	Present work			Maruyama, *et al.*
	ρ	$\lvert A\rvert$ calcd.	$\lvert A\rvert$ obs.[a]	$\lvert A\rvert$ obs.
1, 8	0.1216	3.39	3.25[b]	3.70
2, 7	−0.0426	1.15	1.00	0.59
3, 6	0.1152	3.10	3.82[b]	3.70
4, 5	−0.0410	1.11	1.00	0.59
4a, 10a	0.1195			
8a, 9a	−0.0535			
9	0.4744			
10	0.0701			
1′	−0.0060			
2′, 6′	0.0107	0.29	0.50	1.17
3′, 5′	−0.0042	0.11	0.00	0.00
4′	0.0102	0.28	0.19	1.17
θ[c]	72°			—
Temperature	room temperature			room temperature
g-value	2.0068			—
Parameters	$\alpha_{Se}=\alpha+\beta$, $\alpha_{adj}=\alpha+0.1\beta$, $\beta_{Se}=0.5\beta$, $\lambda=1.2$			—

a) The ESR spectra were measured on a Universal-Cavity TE_{105} of 3B type Spectrometer manufactured by Japan Electron Optics Lab. Co., Ltd.

b) In analogy with 9-phenylxanthyl radical, $A_{3,6H(obs.)}$ can be assigned to a larger value than $A_{1,8H(obs.)}$, though $A_{1,8H(calcd.)}$ is larger than $A_{3,6H(calcd.)}$ according to the results of MO calculation. Refer to M.D. Sevilla and G. Vincow, *J. Chem. Phys.*, **72**, 3641 (1968) and M. Hori, T. Kataoka, Y. Asahi, and E. Mizuta, *Chem. Pharm. Bull.* (Tokyo), **21**, 1692 (1973).

c) Angle between the plane of the 9-phenyl group and that of the thioxanthyl moiety: by the relation $\beta_{9-1'}=\beta\cos\theta$.

TABLE II. Proton Hyperfine Splitting Constants ($\lvert A_{iH}\rvert$) of 9-Phenyl(-d_5)selenoxanthyl Radical (X)

Position	1, 8	2, 7	3, 6	4, 5	θ	Temperature
$\lvert A\rvert$ obs.	3.20[a]	1.05	3.82[a]	1.05	72°	room temperature

a) See Table I. footnote.[b]

2. In our previous report,[1] 9,9′-diselenoxanthenyl (XI) was obtained with a yield of 13 % besides 10-phenyl-10-selenaänthracene (IIIa) by the reaction between selenoxanthylium perchlorate (IIa) and phenyllithium as shown Chart 3. Although this result is explained by the mechanism as shown in Chart 4, experimental results show that phenol is not formed. Therefore, the appreciable yield of XI obtained from IIa along with IIIa can be explained only by a radical mechanism. It is likely that a radical mechanism is related to the reaction between II and organometallic compounds to a considerable degree. Selenoxanthyl radical is formed in this case as an intermediate.

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5) K. Maruyama, M. Yoshida, and K. Murakami, *Bull. Chem. Soc. Japan*, 43, 152 (1970).
6) M. Gomberg and L.H. Cone, *Ann.*, 376, 201 (1910).

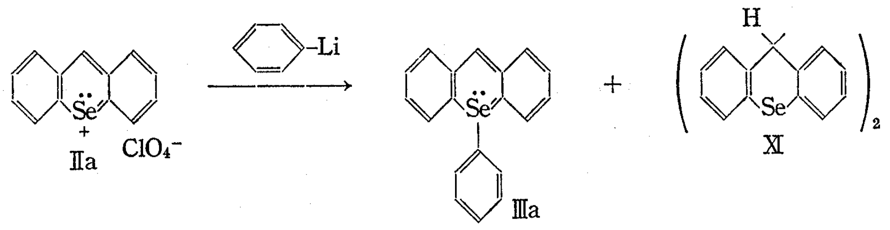

Chart 3

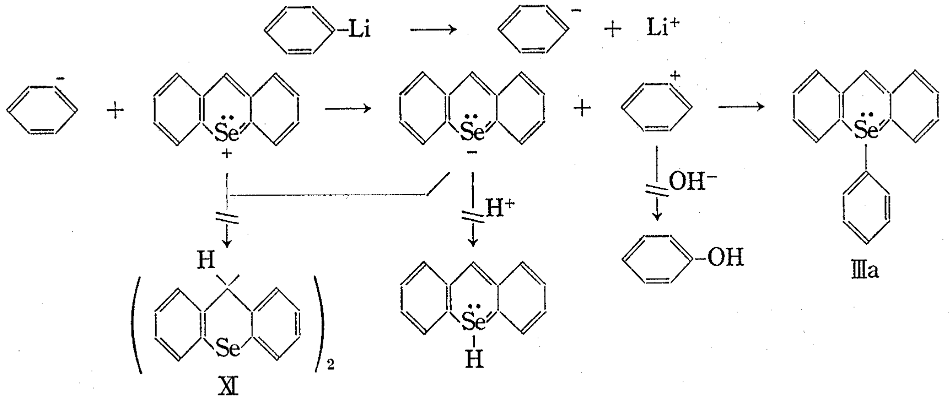

Chart 4

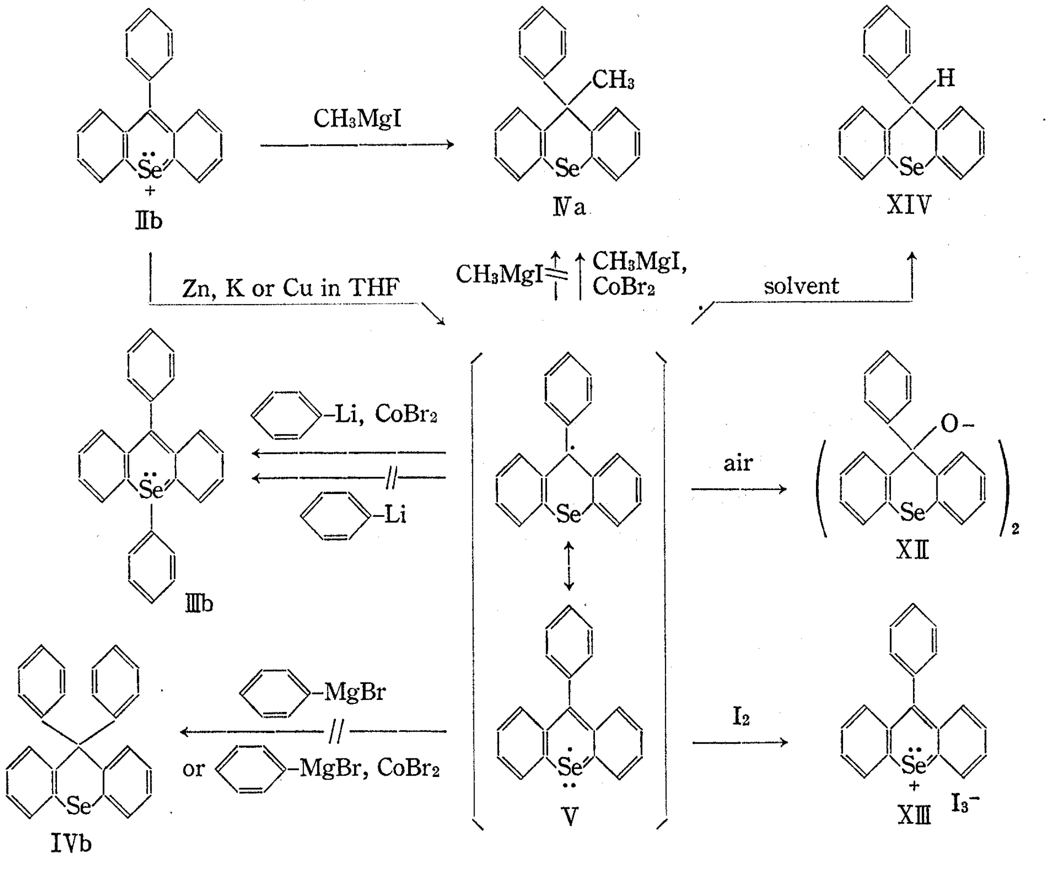

Chart 5

3. From the reason as mentioned above, the authors then closely examined chemical reactivities of the stable radical (V). Results are as follows (Chart 5):
Although V which was synthesized by the one electron reduction of IIb in THF under nitrogen was stable, it abstracted hydrogen from the solvent to form 9-phenylselenoxanthene (XIV) and also formed 9-phenylselenoxanthenyl peroxide (XII) with a yield of 66% when

dry air was blown into it. V was also reacted with an ethereal solution of iodine to form 9-phenylselenoxanthylium triiodide (XIII), with a yield of 60%. V reacted with none of various Grignard reagents and phenyllithium but reacted with the solvent to form XIV only as mentioned above. However, a similar reaction gave different results depending upon the kind of the reagent in the presence of cobaltous bromide, which caused a radical reaction of Grignard reagents. When V was allowed to react with phenylmagnesium bromide in the presence of cobaltous bromide, expected products were not formed, and XIV only was formed. However, 9,10-diphenyl-10-selenaänthracene (IIIb) was formed with a yield of 14% in the case of phenyllithium. This difference in the reactivity is explained as follows: The reaction between phenylmagnesium bromide takes place in a solvent cage resulting in the formation of biphenyl only. The phenyl radical formed by the reaction between phenyllithium and cobaltous bromide couple with V outside the solvent cage and gives IIIb.

On the other hand, the reaction of methylmagnesium iodide with V gave IVa in the presence of cobaltous bromide with a yield of 28%. Therefore, it was found that the reaction took place outside the solvent cage contrary to the reaction of phenylmagnesium bromide.7)

4. The authors could not recognize any of 9-phenyl-10-substituted selenoxanthenium salts, such as XV and XVII, by the treatment of IIb with various organometallic reagents. Although the reactions of XV or XVII with a strong base in ether are explained as an ionic mechanism by ESR measurement, these reactions do not give any of selenaänthracene derivatives (III) as shown in Chart 6.

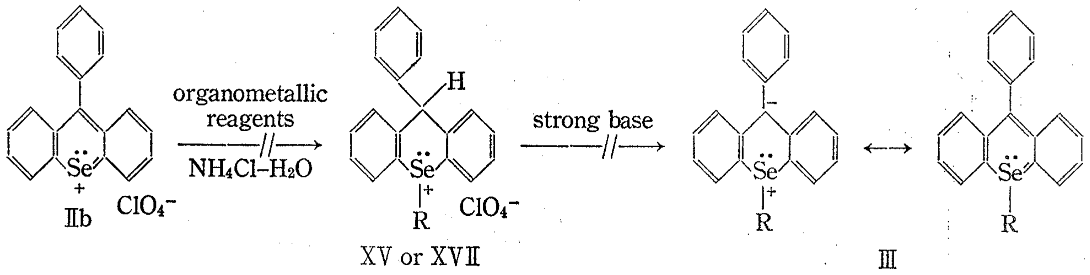

Chart 6

Chart 7 explains in closer detail the results shown in Chart 6. XIV reacts with 35% H_2O_2 in a mixture of dichloromethane-acetic acid and gives 9-phenylselenoxanthene 10-oxide (XVI) in a yield of 80% at room temperature. The presence of the geometrical isomers of XVI was not noticed by the nuclear magnetic resonance (NMR) spectrum in $CDCl_3$. Treatment of XVI with methylmagnesium iodide in ether gives 9-methyl-9-phenylselenoxanthene (IVa), mp 186°. 10-Methyl-9-phenylselenoxanthenium fluoroborate (XV) was synthesized by the reaction between XIV and methyl iodide in the presence of silver fluoroborate. XV reacted with dimsyl anion (DMSO–NaH) in dimethylsulfoxide under nitrogen to form XIV and IVa with a ratio of yield in 50/1. This reaction is accompanied by the formation of some carbene. Namely, the presence of norcarane was found in the reaction products by gas chromatography on 20% DEGS on Chromosorb W column when the reaction was performed in the presence of cyclohexene. XVI reacted with anisole in the presence of phosphorus oxychloride and 70% perchloric acid at 0° and gave 10-(*p*-methoxyphenyl)-9-phenylselenoxanthenium perchlorate (XVII) which shows double melting points of 188° and 245°, and IIb in the yields of 77% and 10%, respectively. IIb is converted to 9-methoxy-9-phenylselenoxanthene by the recrystallization from methanol. As is suggested by the double melting points, XVII was a mixture of two geometrical isomers, which were hardly separated from each

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7) H.M. Relles, *J. Org. Chem.*, **34**, 3687 (1969).

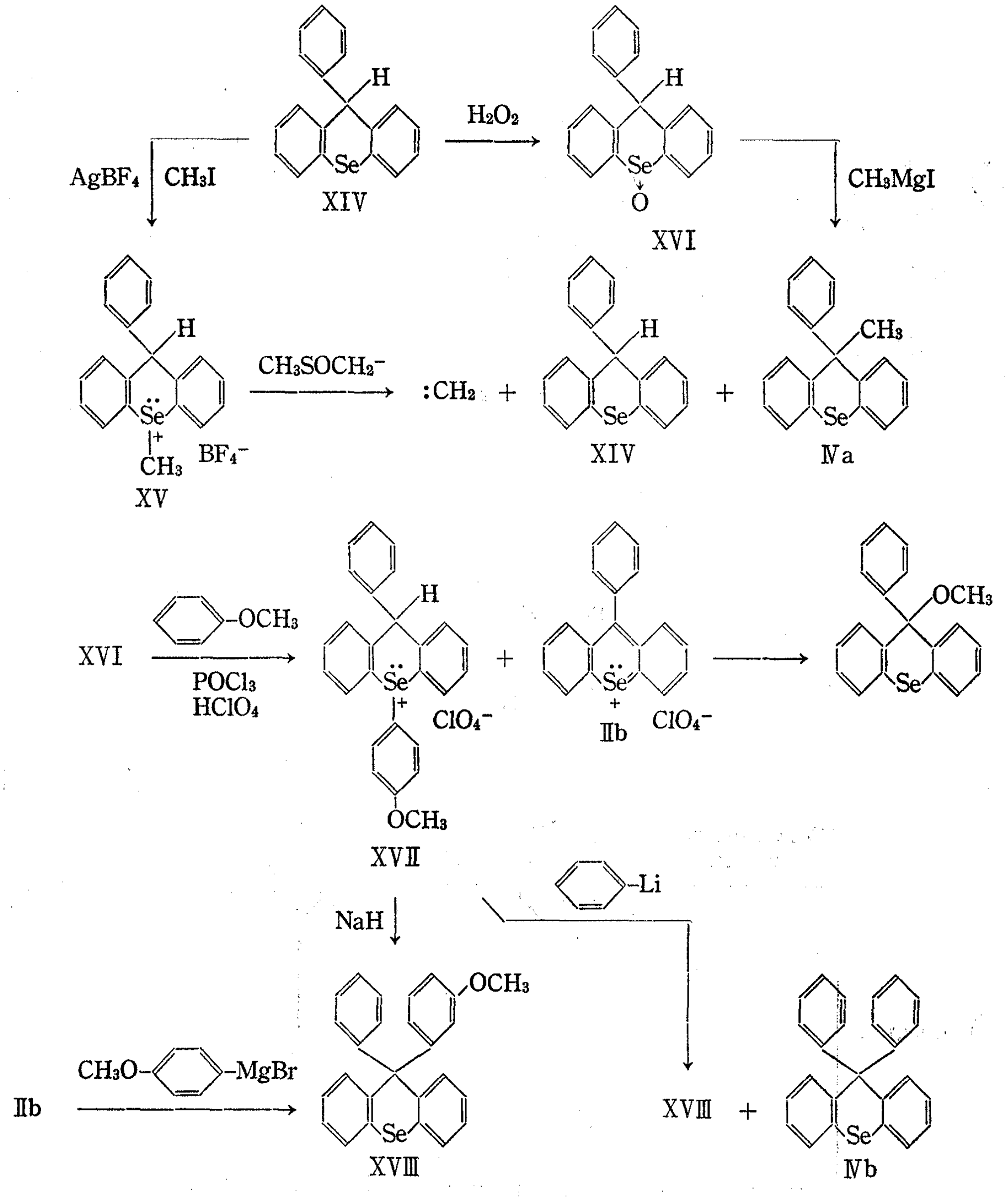

Chart 7

other. The intensity of the NMR spectrum in CF$_3$COOH at following τ values indicated that the ratio of the two isomers, that is, Isomer-1 and Isomer-2, was 2/1. Isomer-1: 1.65—3.55 (17H, multiplet, aromatic H), 4.06 (1H, singlet, C$_9$–H), and 5.94 (3H, singlet, OCH$_3$). Isomer-2: 1.65—3.55 (17H, multiplet, aromatic H), 4.20 (1H, singlet, C$_9$–H), and 6.13 (3H, singlet, OCH$_3$).

Andersen, *et al.*[8] pointed out that such a pair of isomers can be easily converted to each other, because the energy barriers (ΔG) of the pyramidal inversion and the ring inversion are rather small, say about 20—30 kcal/mole, in cyclic sulfonium salts. Very recently, the authors successfully isolated the pair of isomers in the course of study on the sulfonium compounds, though only for a pair, (S$^+$-1) and (S$^+$-2), which shows mp 154° and 211°,[9] as shown in Chart 8 and also confirmed that either of the two gives both of the isomers on recrystallization from *n*-butanol. Details will be published elsewhere on the structures of cyclic selenonium (XVII) and the corresponding sulfonium salts in the near future.

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8) K.K. Andersen, M. Cinquini, and N.E. Papanikolaou, *J. Org. Chem.*, **35**, 706 (1970).

9) M. Hori, T. Kataoka, and H. Shimizu, the 93rd Annual Meeting of the Pharmaceutical Society of Japan, Tokyo, April, 1973, Preprints, II, p. 105.

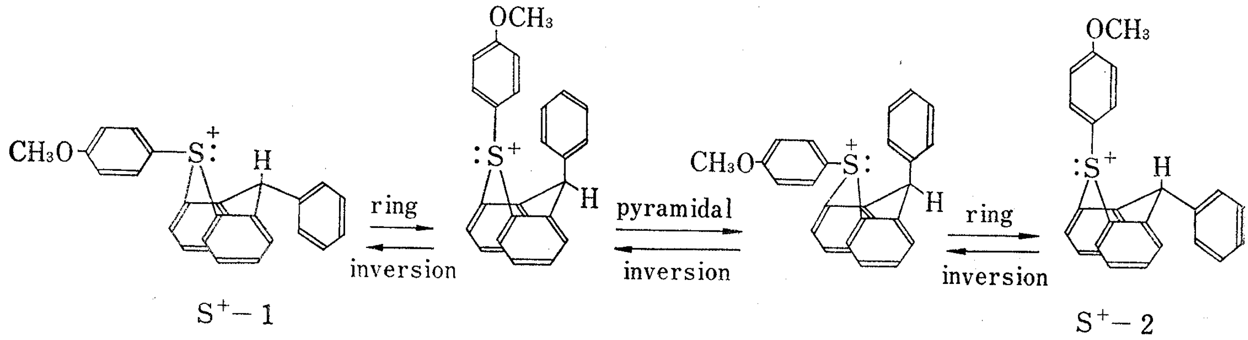

Chart 8

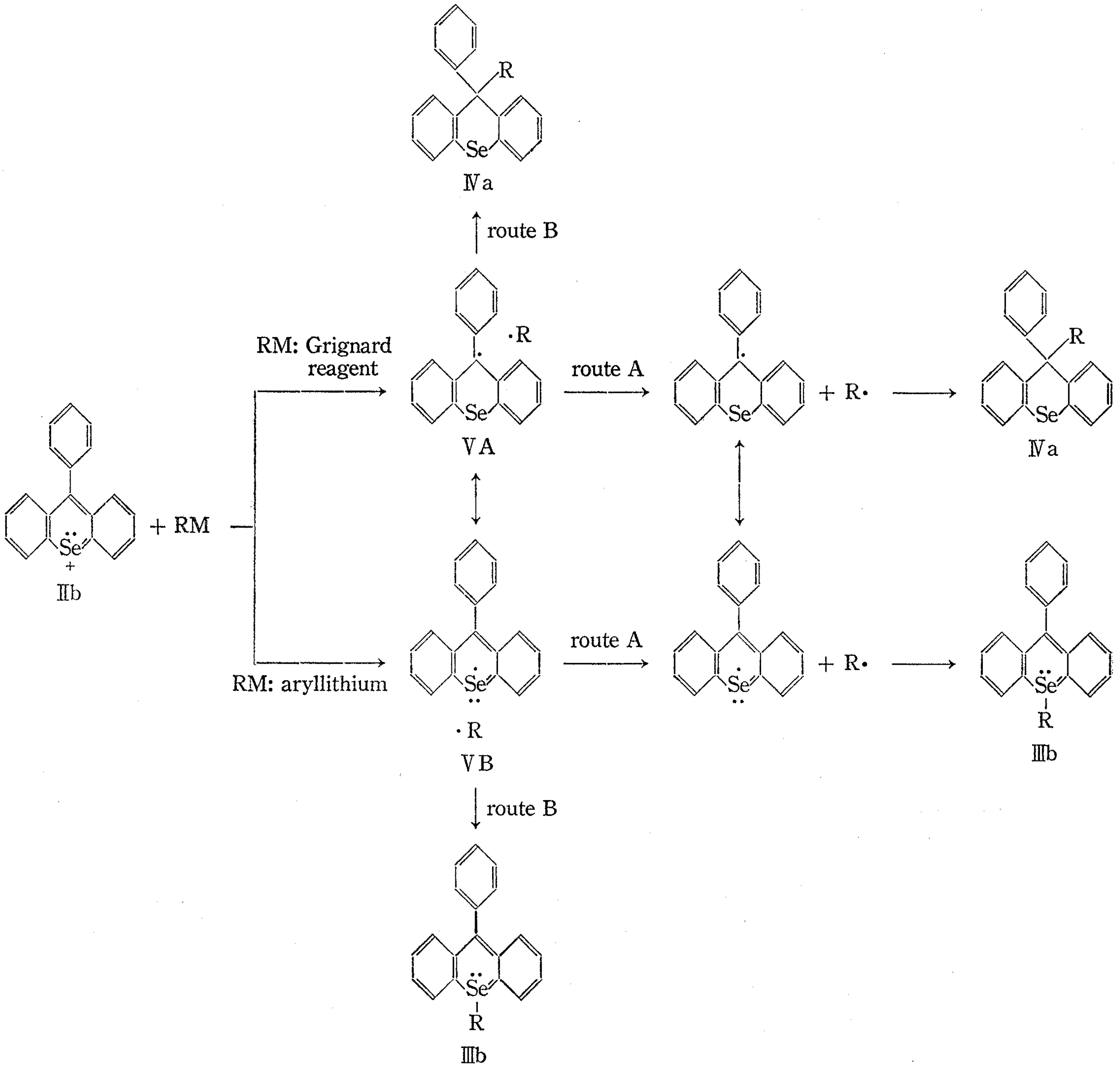

Chart 9

XVII reacted with NaH in THF under nitrogen to form only 9-(*p*-methoxyphenyl)-9-phenylselenoxanthene (XVIII), with a yield of 92%, which was also obtained from IIb and *p*-methoxyphenylmagnesium bromide. XVIII showed mp 208°, NMR ($CDCl_3$)τ: 2.20—3.48 (17H, multiplet, aromatic H) and 6.21 (3H, singlet, OCH_3). However, XVII reacted with phenyllithium in ether under nitrogen to form XVIII and 9,9-diphenylselenoxanthene (IVb), mp 212°, with a yield of 29.4% and 43.9%, respectively. The formation of IVb is clearly explained as a ligand exchange reaction[10] on a selenonium salt.

Mechanism of the Reaction of IIb with Organometallic Reagents

Summarizing the results mentioned above, the authors propose a mechanism as shown in Chart 9 for the reaction between IIb and organometallic reagents.

The reaction between IIb and an organometallic reagent RM forms a radical pair VA or VB. By this formation, it is estimated that a radical pair takes the VA type against Grignard reagents because of the difference in the basicity of RM, but takes the VB type against aryllithium. In the case of methylmagnesium iodide, IVa is mainly formed through route B. IVa is partly formed through route A. On the other hand, the main route of VB is B as in the case of methylmagnesium iodide, and partly forms IIIb through route A. The position of reaction of the radical (V) are 9 and 10. The values of the densities of odd electron, ρ, are 0.4744 and 0.0701, respectively. A question still remains to be solved in the future why aryllithium only couples with the positive selenium of IIb to form selenaänthracene derivatives.

Experimental[11]

9-Phenyl(-d_5)selenoxanthenol (VII)——a) To an ethereal solution of C_6D_5MgBr prepared from C_6D_5Br (3.2 g) and Mg (0.5 g) a suspension of VI[1] (2.6 g) in hot benzene was added. The ether was removed as much as possible. After refluxing for 18 hr the reaction mixture was treated in the usual way. The solid thus obtained was recrystallized from ether–pet. ether to give colorless prisms (3.2 g), mp 105°. *Anal.* Calcd. for $C_{19}H_9D_5OSe$: C, 66.66; H, 5.59. Found: C, 66.53; H, 5.53. IR ν_{max}^{KBr} cm^{-1}: 3250 (OH), 2250 (C–D). b) VIII (0.5 g) was treated with 10% NaOH, and the reaction mixture was extracted with ether. The extract was dried (K_2CO_3) and evaporated. The resulting solid was recrystallized from pet. ether to give colorless prisms (0.2 g). This sample was identified by the comparison of the IR spectrum with that of a sample prepared by the method a).

9-Phenyl(-d_5)selenoxanthylium Perchlorate (VIII)——To a solution of VII (2.5 g) in ether containing a small amount of AcOH, 70% $HClO_4$ was gradually added until no more precipitate appeared. The purple precipitate was filtered and rinsed with dry ether. Recrystallization from $CHCl_3$–pet. ether gave purple plates (2.5 g), mp 173—175° (decomp.). *Anal.* Calcd. for $C_{19}H_{15}D_5O_4ClSe$: C, 53.72; H, 4.27. Found: C, 53.80; H, 4.33. IR ν_{max}^{KBr} cm^{-1}: 2250 (C–D), 1100 (ClO_4^-).

9-Phenyl(-d_5)selenoxanthene (IX)——To a suspension of $LiAlH_4$ (0.3 g) in ether, VIII (0.3 g) was added with stirring. After refluxing for 2 hr, the reaction mixture was treated with a saturated NH_4Cl solution and extracted with ether. The extract was dried (K_2CO_3) and evaporated. The resulting solid was recrystallized from MeOH to give colorless prisms (0.1 g, 43.3%), mp 114—115°. *Anal.* Calcd. for $C_{19}H_9D_5Se$: C, 69.93; H, 5.87. Found: C, 69.93; H, 5.90. IR ν_{max}^{KBr} cm^{-1}: 2250 (C–D). NMR ($CDCl_3$) τ: 2.50—3.00 (8H, multiplet, aromatic H), 4.60 (1H, singlet, C_9–H).

Reaction of 9-Phenylselenoxanthyl Radical (V) with Air——Dry air was passed through a stirred suspension of IIb[1] (1 g) and Zn powder (0.5 g) in THF (15 ml) for 5 hr. The precipitate was filtered and washed with THF thoroughly. After the filtrate was evaporated, the resulting residue was washed with ether and collected by filtration. Recrystallization from benzene–pet. ether gave 9-phenylselenoxanthenyl peroxide (XII) as colorless plates (0.53 g), mp 173° (decomp.). *Anal.* Calcd. for $C_{38}H_{26}O_2Se$: C, 67.86; H, 3.89. Found: C, 68.10; H, 4.03. When a benzene solution of XII was heated for several hours, XII was changed into selenoxanthone.

Reaction of V with Iodine——A suspension of IIb (1.0 g) and Zn powder (1.0 g) in THF (35 ml) was stirred for 30 min under an N_2 stream. Iodine (2.1 g) in ether (100 ml) was added to the radical solution thus prepared. After standing for 1 hr, the solvent was removed under reduced pressure. The residue was washed with benzene and hot AcOH and recrystallized from CH_3CN to give 9-phenylselenoxanthylium triiodide (XIII) as purple prisms (1.1 g, 60%), mp 161—163° (decomp.). *Anal.* Calcd. for $C_{19}H_{13}I_3Se$: C, 32.55; H, 1.87. Found: C, 32.83; H, 1.95.

Hydrogen Abstraction by V from Solvent——A suspension of IIb (1.0 g) and Zn powder (0.5 g) in THF (30 ml) was stirred for 2 hr under an N_2 stream, and then added with anhydrous ether (30 ml). Stirring

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[10] For the mechanism of ligand exchange reactions on the cyclic sulfonium compounds, M. Hori, T. Kataoka, H. Shimizu, and M. Miyagaki, *Chemistry Lett.*, **1972**, 515.

[11] All melting points are uncorrected.

was continued for a day, and dry air was blown into the reaction mixture to convert remaining V into peroxide (XII). After removal of the solvent, the residue was washed with ether. Evaporation of the washings afforded 9-phenylselenoxanthene (XIV) (0.40 g), mp 117°, which was recrystallized from pet. ether as colorless needles. An ether-insoluble material was extracted with benzene. Removal of the solvent gave XII (0.2 g).

Reactions of V with Organometallic Reagents (CH_3MgI, C_6H_5MgBr, and C_6H_5Li)——V was prepared from IIb (2 g) and Zn powder (1 g) in THF (35 ml) as mentioned above. To a filtered solution of V, the organometallic reagent (5 equivalents of IIb) was added under an N_2 stream. After standing for a day, the reaction mixture was decomposed with a cold NH_4Cl solution and extracted with ether. The extract was dried (K_2CO_3) and evaporated. The residue was chromatographed on silica gel to give XIV (0.40—0.47 g) and XII (*ca.* 0.03 g).

Reaction of V with Methylmagnesium Bromide in the Presence of $CoBr_2$——To a filtered solution of V prepared from IIb (2 g) and Zn powder (1 g) in THF (35 ml), an ethereal solution of CH_3MgI (5 equivalents of IIb) was added under an N_2 stream. Anhydrous $CoBr_2$ (0.2 g) was then added. After standing for a day, the reaction mixture treated in the usual manner gave 9-methyl-9-phenylselenoxanthene (IVa) (0.4 g) and a small amount of XII.

Reaction of V with Phenylmagnesium Bromide in the Presence of $CoBr_2$——To an ethereal solution of C_6H_5MgBr (5 equivalents of IIb), a filtered solution of V prepared from IIb (2.0 g) and Zn powder (1 g) was added under an N_2 stream. After standing for a day, the reaction mixture worked up as mentioned above gave XIV (0.6 g) and biphenyl.

Reaction of V with Phenyllithium in the Presence of $CoBr_2$——An ethereal solution of C_6H_5Li (5 equivalents of IIb) was added to a filtered solution of V prepared from IIb (2 g) and zinc powder (1 g) in THF (35 ml) under an N_2 stream. Anhydrous $CoBr_2$ (0.2 g) was then added. After standing for 10 hr, the reaction mixture was treated in the usual way to give 9,10-diphenyl-10-selenaänthracene (IIIb) (0.3 g, 14%) as brown powders. This compound had the same IR, NMR, and Mass spectra as those of an authentic sample.

9-Phenylselenoxanthene 10-oxide (XVI)——To a solution of XIV (1.8 g) in a mixture of CH_2Cl_2 (10 ml) and AcOH (10 ml) 35% H_2O_2 (0.6 g) was gradually added with stirring. After standing for 3 days, the mixture was poured into ice-water and extracted with CH_2Cl_2. The extract was washed with dil. $NaHCO_3$, dried (K_2CO_3), and evaporated. Ether was added to the residue and then the resulting crystals were collected. Recrystallization from ether gave colorless prisms (1.5 g, 80%), mp 160°. *Anal.* Calcd. for $C_{19}H_{14}OSe$: C, 67.65; H, 4.19. Found: C, 67.78; H, 4.21. IR ν_{max}^{KBr} cm^{-1}: 825 (Se–O). NMR ($CDCl_3$) τ: 1.70—2.10 (2H, multiplet, aromatic H ($C_{1,8}$–H)), 2.20—3.23 (11H, multiplet, aromatic H), 6.40 (1H, singlet, C_9–H).

Reaction of XVI with Methylmagnesium Iodide——To an ethereal solution of CH_3MgI prepared from CH_3I (2.6 g) and Mg (0.5 g), a benzene solution of XVI (0.93 g) was added under an N_2 stream. After refluxing for 10 hr, the cooled reaction mixture was decomposed with 24% HBr (50 ml) and extracted with benzene. The extract was washed with dil. Na_2CO_3, dried (K_2CO_3), and evaporated into 9-methyl-9-phenylselenoxanthene (IVa) and 9-phenylselenoxanthene (XIV) by chromatography on silica gel. IVa (0.36 g, 59.7%), mp 186°, was recrystallized from ether. *Anal.* Calcd. for $C_{20}H_{16}Se$: C, 71.67; H, 4.81. Found: C, 71.58; H, 4.71. XIV (0.24 g, 40.4%), mp 117°, was recrystallized from pet. ether. *Anal.* Calcd. for $C_{19}H_{14}Se$: C, 71.02; H, 4.39. Found: C, 70.92; H, 4.41.

10-Methyl-9-phenylselenoxanthenium Fluoroborate (XV)——$AgBF_4$ (1.0 g) was gradually added to a mixture of XIV (0.9 g) and CH_3I (18 ml) at an ice-bath temperature with stirring. After the reaction mixture was allowed to stand overnight, the resulting precipitate was filtered off and washed thoroughly with CH_2Cl_2. The filtrate and the washings were combined and evaporated. Recrystallization of the residual solid from CH_2Cl_2-ether gave colorless prisms (1.10 g, 92.4%), mp 192°. *Anal.* Calcd. for $C_{19}H_{17}BF_4Se$: C, 56.77; H, 4.05. Found: C, 56.57; H, 3.80. IR ν_{max}^{KBr} cm^{-1}: 1150 (BF_4^-). NMR (CF_3COOH) τ: 1.80—3.26 (13H, multiplet, aromatic H), 4.14 (1H, singlet, C_9-H), 6.51 (3H, singlet, CH_3).

Reaction of XV with Sodium Methylsulfinylmethide (Dimsyl Anion)——A solution of sodium methylsulfinylmethide was prepared from freshly distilled DMSO (3 ml) and 50% NaH (dispersed in mineral oil) (60 mg) at 70—75° under an N_2 stream. To the yellow solution thus prepared, a mixture of XV (1.0 g), cyclohexene (10 ml), and DMSO (5 ml) was gradually added. The reaction mixture turned reddish brown. The reaction was continued for 2 hr. After standing overnight, the solution was poured into ice-water and extracted with $CHCl_3$. The extract was washed with water for several times, dried ($MgSO_4$), and evaporated. The residue was separated into 9-phenylselenoxanthene (XIV) and 9-methyl-9-phenylselenoxanthene (IVa). XIV (0.42 g), mp 117°, was recrystallized from pet. ether. *Anal.* Calcd. for $C_{19}H_{14}Se$: C, 71.03; H, 4.40. Found: C, 71.32; H, 4.50. IVa (0.08 g), mp 186°, was recrystallized from MeOH. *Anal.* Calcd. for $C_{20}H_{16}Se$: C, 71.64; H, 4.81. Found: C, 71.46; H, 4.65. These samples were identified by the comparison of the IR spectra with those of authentic samples. Norcarane was detected from the extract by glc and identified by the comparison of the retention time with that of an authentic sample.12)

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12) Gas chromatography (GLC) was carried out by the use of JEOL model JGC-1100 gas chromatography equipped with hydrogen flame ion detector. A 1 m column charged with 20% DEGS absorbed on Chromosorb W was used.

10-(*p*-Methoxyphenyl)-9-phenylselenoxanthenium Perchlorate (XVII)——To a cold mixture of $POCl_3$ (2 ml), 70% $HClO_4$ (4 ml), and anisole (0.8 g) XVI (1.5 g) was gradually added with stirring for a day in an ice-bath, the reaction mixture was poured into ice water and stirred for 30 min. The supernatant solution was decanted, and ether was added to the residual oil with stirring. The resulting solid was collected by filtration and rinsed with ether. Recrystallization from MeOH gave colorless prisms (1.8 g, 77%), mp 188° and 245°. *Anal.* Calcd. for $C_{26}H_{21}O_5ClSe$: C, 59.13; H, 4.01. Found: C, 58.80; H, 4.10. NMR (CF_3COOH) τ: 1.65—3.55 (multiplet, aromatic H), two pairs of peaks at 4.06 (singlet, C_9-H), 5.94 (singlet, OCH_3) and 4.20 (singlet, C_9-H), 6.13 (singlet, OCH_3). The product ratio of the former/the latter is 2/1. From the MeOH mother liquor, 9-methoxy-9-phenylselenoxanthene (0.15 g, 10%) was obtained.

Reaction of XVII with Sodium Hydride——To a suspension of XVII (0.53 g) in THF (30 ml), 50% NaH (dispersed in mineral oil) (79 mg) was added with stirring under an N_2 stream. After stirring for 5 hr the solvent was evaporated under reduced pressure, and water was added to the residue. The mixture was extracted with benzene. The extract was dried ($MgSO_4$) and evaporated. The resulting solid was recrystallized from benzene–pet. ether to give 9-(*p*-methoxyphenyl)-9-phenylselenoxanthene (XVIII) as colorless prisms (0.39 g, 92%), mp 208°. *Anal.* Calcd. for $C_{26}H_{20}OSe$: C, 73.29; H, 4.84. NMR ($CDCl_3$) τ: 2.20—3.48 (17H, multiplet, aromatic H), 6.21 (3H, singlet, OCH_3). This sample was identified by the comparison of the IR spectrum with that of an authentic sample.

Reaction of IIb with *p*-Methoxyphenylmagnesium Bromide——To an ethereal solution of *p*-$CH_3OC_6H_4$-MgBr prepared from *p*-bromoanisole (0.8 g) and Mg (0.1 g), IIb was added under an N_2 stream. After refluxing for 3 hr, the reaction mixture was decomposed with dil. NH_4Cl and extracted with benzene. The extract was dried ($MgSO_4$) and evaporated. The resulting solid was purified by column chromatography and recrystallized from MeOH–benzene to give XVIII as colorless prisms (0.44 g, 51%), mp 208°. *Anal.* Calcd. for $C_{26}H_{20}OSe$: C, 73.06; H, 4.71. Found: C, 72.98; H, 4.68.

Reaction of XVII with Phenyllithium——To a suspension of XVII (0.53 g) in ether, an excess C_6H_5Li was added under an N_2 stream. After stirring for 5 hr, the reaction mixture was decomposed with a cold NH_4Cl solution and extracted with ether. The extract was dried (K_2CO_3) and evaporated. The residue was separated into 9-(*p*-methoxyphenyl)-9-phenylselenoxanthene (XVIII) and 9,9-diphenylselenoxanthene (IVb) by preparative TLC using benzene–*n*-hexane (1:5). IVb (0.175 g, 43.9%), mp 212°, which has a large *Rf* value, was identified by comparisons of the IR spectrum and the melting point with those of an authentic sample. *Anal.* Calcd. for $C_{25}H_{18}Se$: C, 75.56; H, 4.57. Found: C, 75.73; H, 4.67. XVIII (0.126 g, 29.4%), which has a small *Rf* value, was identified by comparisons of the IR spectrum and the melting point with those of an authentic sample.