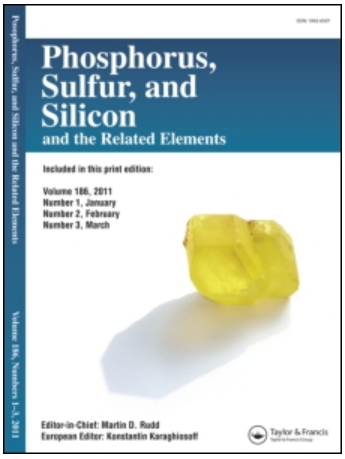

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

CHEMISTRY OF *CIS*- AND *TRANS*-9-PHENYLSELENOXANTHENE-*N*-ARYLSULFONYLSELENILIMINES[1]

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To cite this Article Tomimatsu, Kiminori , Kataoka, Tadashi , Shimizu, Hiroshi and Hori, Mikio(1983) 'CHEMISTRY OF *CIS*- AND *TRANS*-9-PHENYLSELENOXANTHENE-*N*-ARYLSULFONYLSELENILIMINES[1]', Phosphorus, Sulfur, and Silicon and the Related Elements, 16: 1, 97 — 110
To link to this Article: DOI: 10.1080/03086648308077757
URL: http://dx.doi.org/10.1080/03086648308077757

Phosphorus and Sulfur, 1983, Vol. 16, pp. 97–110
0308-664X/83/1601-0097/$18.50/0

CHEMISTRY OF *CIS*- AND *TRANS*-9-PHENYLSELENOXANTHENE-*N*-ARYLSULFONYLSELENILIMINES[1]

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(*Received January 24, 1983*)

cis- and *trans*-9-Phenylselenoxanthene-*N*-(arylsulfonyl)selenilimines were synthesized and isolated. Their stereochemistry was ascertained from the NMR spectra. Cis isomers reacted with chloramine-T or -B by an S_N2 type substitution to form trans isomers, but the reverse reaction did not take place. When trans isomers were refluxed in toluene they underwent intermolecular 1,4 rearrangement to give 9-arylsulfonamido-9-phenylselenoxanthene. The cis isomers neither rearranged nor isomerized. On treatment with DABCO, both isomers rearranged intermolecularly to 9-(*N*-arylsulfonamido)selenoxanthenes at room temperature. Hydrolysis of both isomers yielded *trans*-9-phenylselenoxanthene 10-oxide. Reactions with *p*-methoxyphenylmagnesium bromide or methylmagnesium iodide afforded 9-(*p*-methoxyphenyl)-9-phenylselenoxanthene or 9-phenylselenoxanthene as a main product, respectively.

Recently organoselenium compounds have played an increasingly important role in synthetic organic chemistry. One of the major applications of organoselenium chemistry is based on the fact that selenoxides can be converted into olefins under very mild conditions.[2] However, little attention has been paid to the organic chemistry of hypervalent selenium compounds. Selenilimines of cyclic selenium compounds were synthesized by the Oae and Hellwinkel groups.[3] The stereochemistry of the selenilimines has not been studied so far. We wish to report on the synthesis of 9-phenylselenoxanthene selenilimines, their stereochemistry and their reactions.

RESULTS AND DISCUSSION

Synthesis: The starting materials for the selenilimines, 9-phenylselenoxanthenes were prepared by a more convenient method than that reported previously[4] as shown in Scheme 1. 2-Phenylselenobenzaldehyde (**1**) was synthesized from sodium benzeneselenolate and 2-chlorobenzaldehyde in 86.1% yield. Reaction of **1** with phenylmagnesium bromide gave 2-(phenylseleno)phenylphenylmethanol (**3a**) in 98.7% yield. Cyclization of **3a** with 80 v/v% sulfuric acid yielded 9-phenylselenoxanthene (**4a**) (78.6%) together with bis-[2-(diphenylmethyl)phenyl]diselenide (**5a**) (10.8%). The analogous pentadeuteriophenyl derivative (**5b**) was obtained in a similar way. 2-Chloro-9-phenylselenoxanthene (**4c**) was prepared by cyclization of 5-chloro-2-(phenylseleno)phenylphenylmethanol (**3c**) which is available from 5-chloro-2-(phenylseleno)benzophenone (**2**). The structure of the side-product **5a** was

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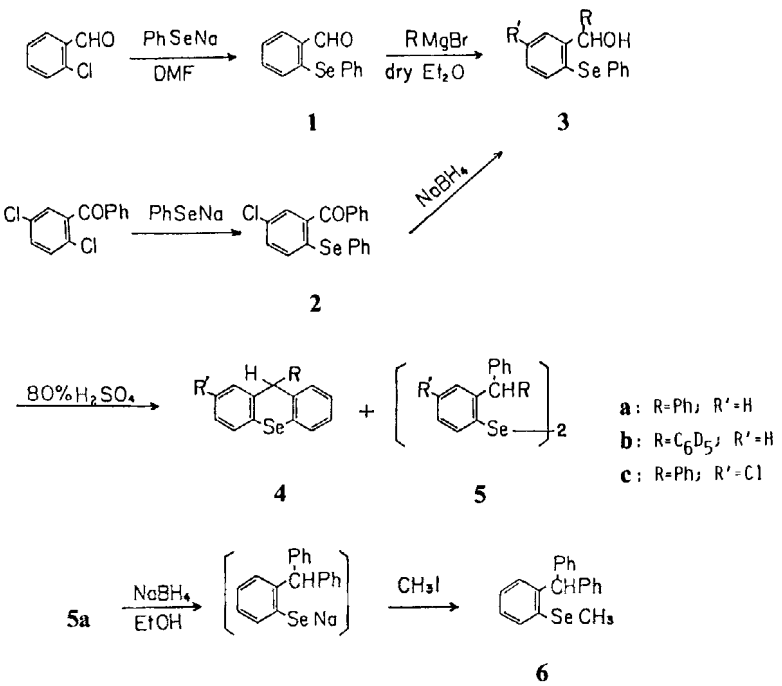
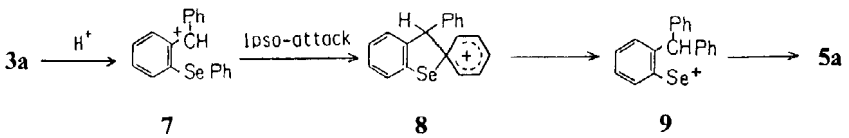


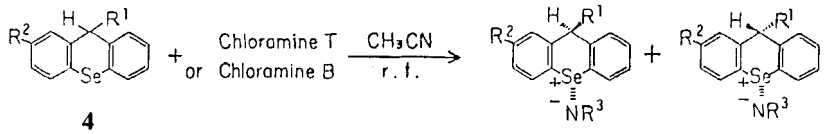
SCHEME 1

confirmed by its spectral and chemical evidences. The NMR spectrum showed a methine proton at δ 5.98 as a singlet. Its molecular formula was $C_{38}H_{30}Se_2$ on the basis of its mass spectrum and elemental analysis. The compound **5a** was reduced with sodium borohydride followed by methylation with iodomethane to give 2-methylselenophenyldiphenylmethane (**6**).

The mechanism of formation of **5a** is outlined in Scheme 2. The carbonium ion (**7**) formed from the methanol (**3a**) by protonation may attack the *ipso*-position of the phenylseleno nucleus to give the spiro intermediate (**8**), which suffers Se—C bond fission to form the selenenium ion (**9**) leading to the diselenide (**5a**). Capozzi and co-workers proposed a similar spiro intermediate in the acid-catalyzed cyclization of 2-arylthiophenylphenylmethanol.[5] The S—C bond is broken in the spiro intermediate of the sulfur compound and the successive 1,2-sulfur shift leads to the isomerized thioxanthene. However, the selenium compound does not cause the 1,2-selenium shift but the selenenium ion **9** is formed because a selenenium ion may be more stable than the corresponding sulfenium ion. The selenenium ion **9** gives diselenide **5a**.



SCHEME 2



4

trans-**10** cis-**10**

a: R^1=Ph; R^2=H; R^3=Ts
b: R^1=Ph; R^2=H; R^3=Bs
c: R^1=C_6D_5; R^2=H; R^3=Bs
d: R^1=Ph; R^2=Cl; R^3=Bs
Ts=p-toluenesulfonyl
Bs=benzenesulfonyl

SCHEME 3

9-Arylselenoxanthene-*N*-(arylsulfonyl)selenilimines (**10**) were prepared by the reaction of 9-arylselenoxanthenes (**4**) with chloramine-T trihydrate or chloramine-B dihydrate in acetonitrile. Isomer ratios and yields are summarized in Table I and physicochemical data are shown in Table II. As shown in Table I, the product ratio of cis and trans isomers changed with the ratio of **4** and chloramine-T or -B. Product ratio, trans/cis was about 1 using 1 eq. of chloramine-T or -B, whereas the ratio, trans/cis was more than 10 using 2 eq. of chloramine-T or -B.

TABLE I

Reactions of 9-phenylselenoxanthene (**4**) and chloramine-T or chloramine-B

Mole Ratio of **4** and Chloramine-T or -B	Yield[a] (%)	Ratio of Products[b]
1 : 1	82.3	*trans-/cis*-**10a** ≒ 1
1 : 2	67.4	*trans-/cis*-**10a** > 10
1 : 1	81.8	*trans-/cis*-**10b** ≒ 1
1 : 2	69.2	*trans-/cis*-**10b** > 10
1 : 1	80.0	*trans-/cis*-**10c** ≒ 1
1 : 2	68.4	*trans-/cis*-**10d** > 10

[a]Isolated yield. Yields are better than those reported in Ref. 1.
[b]The ratio of trans/cis was determined in comparison with the C_9—H intensities of their NMR spectra.

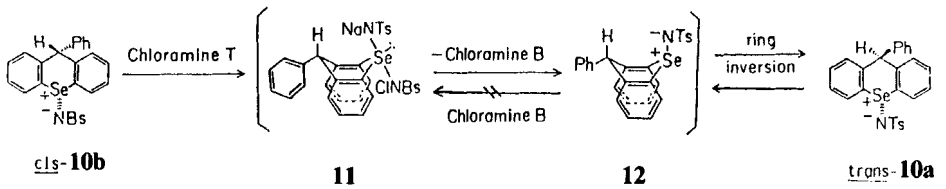
This finding suggested that cis selenilimine initially formed was attacked on the selenium atom by another chloramine-T or -B to form an S_N2 type intermediate (**11**) and was transformed into the more stable trans isomer. This was demonstrated by the reactions in which *cis*-9-phenylselenoxanthene-*N*-(benzenesulfonyl)selenilimine (*cis*-**10b**) reacted with 1 eq. of chloramine-T to afford the S_N2 substitution product (*trans*-**10a**) in good yield, whereas *trans*-**10a** did not react with chloramine-B. The change in configuration can be explained as shown in Scheme 4.

TABLE II

9-Arylselenoxanthene-*N*-(arylsulfonyl)selenilimines

Compd. No.	mp (°C) (dec.)	Appearance	Formula	Analysis (%) Calcd. (Found) C	H	N	NMR ($CDCl_3$) δ
trans-**10a**	173–176	colorless prisms	$C_{26}H_{21}NO_2SSe$	63.67 (63.79	4.32 4.21	2.86 2.83)	2.39 (3 H, s, CH_3), 5.58 (1 H, s, C_9—H), 6.60–6.90 (2 H, m, $C_{2,6}$—H of C_9—Ph), 7.00–7.70 (11 H, m, ArH), 7.75–8.10 (4 H, m, $C_{4,5}$—H and $C_{2,6}$—H of SO_2Ph)
cis-**10a**	190–193	colorless prisms	$C_{26}H_{21}NO_2SSe$	63.67 (63.50	4.32 4.27	2.86 2.86)	2.38 (3 H, s, CH_3), 5.13 (1 H, s, C_9—H), 7.05–7.60 (13 H, m, ArH), 7.65–8.10 (4 H, m, $C_{4,5}$—H and $C_{2,6}$—H of SO_2Ph)
trans-**10b**	171–174	colorless prisms	$C_{25}H_{19}NO_2SSe$	63.02 (63.29	4.02 3.92	2.94 2.96)	5.59 (1 H, s, C_9—H), 6.60–6.90 (2 H, m, $C_{2,6}$—H of C_9—Ph), 7.05–7.70 (12 H, m, ArH), 7.80–8.20 (4 H, m, $C_{4,5}$—H and $C_{2,6}$—H of SO_2Ph)
cis-**10b**	194–198	colorless prisms	$C_{25}H_{19}NO_2SSe$	63.02 (63.09	4.02 4.09	2.94 2.98)	5.12 (1 H, s, C_9—H), 7.05–7.65 (14 H, m, ArH), 7.70–8.15 (4 H, $C_{4,5}$—H and $C_{2,6}$—H of SO_2Ph)
trans-**10c**	172–176	colorless prisms	$C_{25}H_{14}D_5NO_2SSe$	482.0613[a] (482.0623)			5.62 (1 H, s, C_9—H), 7.25–7.80 (9 H, m, ArH), 7.80–8.20 (4 H, m, $C_{4,5}$—H and $C_{2,6}$—H of SO_2Ph)
cis-**10c**	191–196	colorless prisms	$C_{25}H_{14}D_5NO_2SSe$	482.0613[a] (482.0606)			5.13 (1 H, s, C_9—H), 7.05–7.65 (9 H, m, ArH), 7.70–8.15 (4 H, m, $C_{4,5}$—H and $C_{2,6}$—H of SO_2Ph)
trans-**10d**	165–168	colorless prisms	$C_{25}H_{18}ClNO_2SSe$	58.77 (58.51	3.55 3.47	2.74 2.77)	5.57 (1 H, s, C_9—H), 6.60–6.95 (2 H, m, $C_{4,5}$—H), 7.00–8.20 (15 H, m, Arh)

[a] Determined by high resolution mass spectrometry.



SCHEME 4

The benzenesulfonamido (N—Bs) group of *cis*-**10b** is substituted by the toluenesulfonamido (N—Ts) group via the S_N2 type intermediate (**11**). The cis configuration is converted to the trans configuration (**12**). The trans intermediate (**12**) was ring-inverted into a thermodynamically much more stable conformer (*trans*-**10a**). Chloramine-B cannot attack at the selenium atom of *trans*-**10a** because of steric hindrance by an axial 9-phenyl group.

Stereochemistry: Stereoisomers of 9-phenylselenoxanthene selenilimines can exist in four conformational isomers (A–D) owing to ring inversion and pyramidal inversion. Conformers A and C are cis isomers, and conformers B and D are trans isomers.

From Tamura's extensive investigation of the 9-phenylthioxanthene sulfilimines, the N—Ts or N—Bs group prefers the equatorial conformations (conformers B and C) because of its bulkiness.[6a] If the N—Ts or N—Bs group was in the axial position, the chemical shifts of the axial C_9-proton (C_9—H) or 9-phenyl group would be greatly affected by the anisotropy of the $^+Se—N^-$ group. This was not demonstrated by the NMR spectra of **10**, and therefore, the N—Ts or N—Bs group occupies an equatorial position.

Conformations of the 9-phenyl group and the C_9—H were determined by NMR spectroscopy of the selenilimines (**10**). Ternay *et al.*[7] and we,[8] in the stereochemical studies of thioxanthene 10-oxides, and Tamura *et al.*, in their investigation of the stereochemistry of thioxanthene sulfilimines,[6] showed that broadening of the axial C_9—H signal results from allylic coupling with the peri hydrogens ($C_{1,8}$—H). They

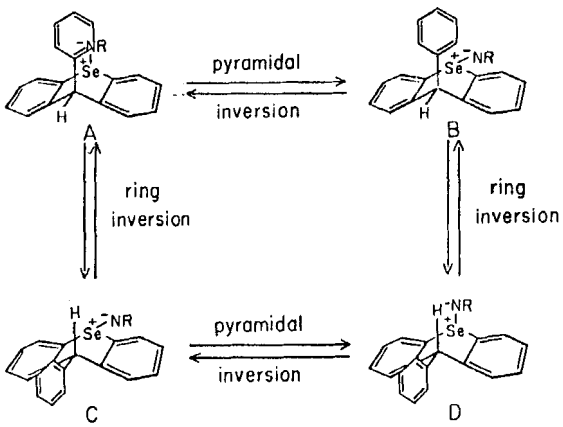


FIGURE 1

also showed that the chemical shifts of the axial C_9—H appears at higher field than those of the equatorial C_9—H mainly because the former is shielded and the latter is deshielded by the thioxanthene ring. The signal of the C_9—H of *cis*-**10b** appeared at δ 5.12 and was 0.47 ppm higher than that of *trans*-**10b** at δ 5.59. Therefore, the C_9—H of *cis*-**10b** occupies the axial position and that of *trans*-**10b** occupies the equatorial position.

On the other hand, if the 9-phenyl group has the axial conformation, the $C_{2,6}$—H of the 9-phenyl group shifts to higher field owing to the shielding effect of the thioxanthene ring. If the 9-phenyl group is equatorial, $C_{1,8}$—H shifts to higher field owing to the shielding effect of the equatorial 9-phenyl group. This generalization can be applied in the selenilimines. To distinguish the signals of the 9-phenyl protons in the NMR spectra from those of other aromatic protons, the NMR spectrum of the 9-pentadeuteriophenyl derivative was measured and compared with those of the corresponding 9-phenyl derivatives. The upfield-shifted $C_{2,6}$—H of the phenyl group of *trans*-**10b** and the $C_{1,8}$—H of *cis*-**10b** were observed at δ 6.60–6.90 and 7.05–7.30, respectively. Thus, the 9-phenyl group of *cis*-**10b** is in the equatorial position and that of *trans*-**10b** is in the axial position.

From the detailed discussion described above, we concluded that trans and cis isomers are conformer B and C, respectively.

Hydrolysis: Selenilimines reported in this paper are stable in the solid state, but both of the cis and trans isomers are hydrolyzed to *trans*-9-phenylselenoxanthene 10-oxide (**13**) on silica gel thin layer chromatography (TLC) plates. In particular, cis isomers were so easily hydrolyzed that they could not be detected on the silica gel TLC plates. The structure of **13** was elucidated by the comparison of its NMR spectrum with that of the corresponding sulfur compound, *trans*-9-phenylthioxanthene 10-oxide, whose structure has been well established[8] (see Figure 2).

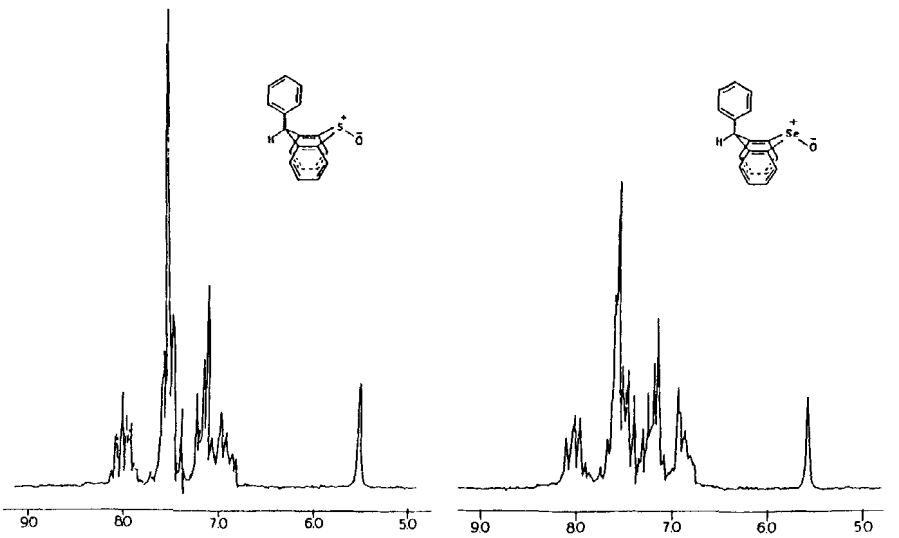
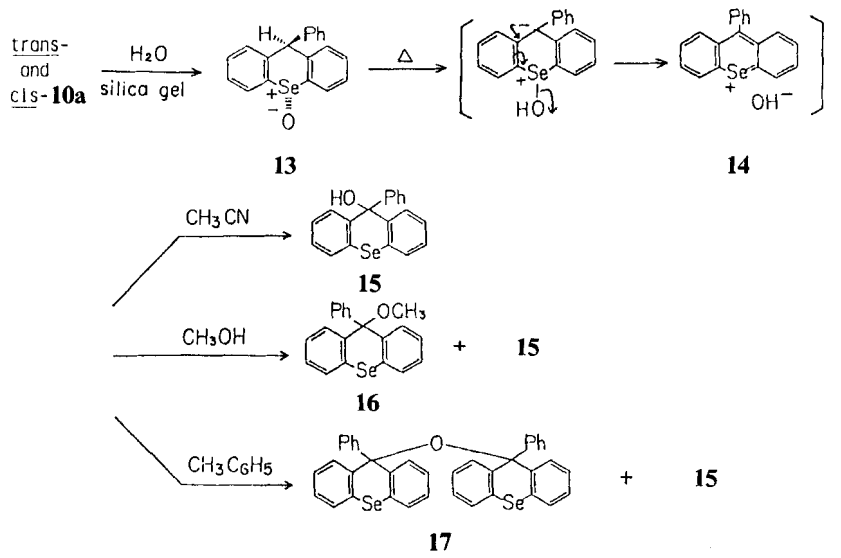


FIGURE 2 NMR spectra of *trans*-9-phenylthioxanthene 10-oxide and *trans*-9-phenylselenoxanthene 10-oxide.



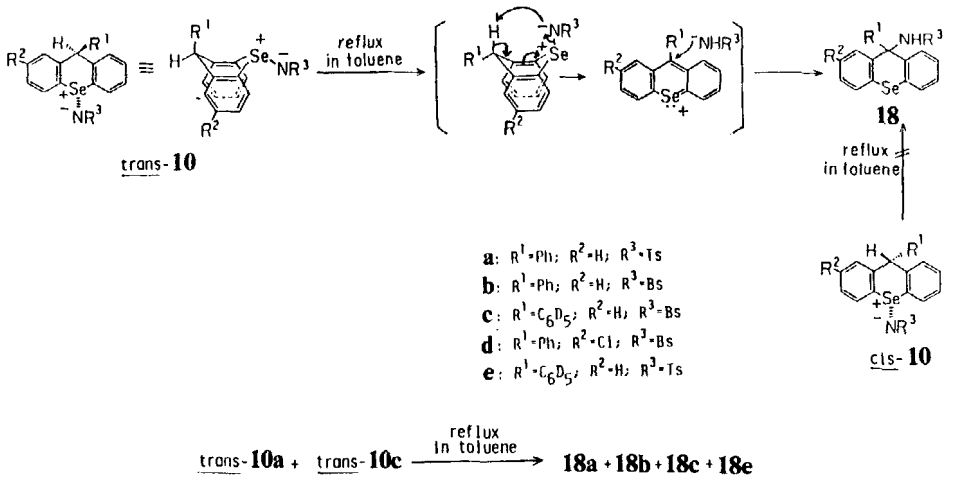
SCHEME 5

The fact that hydrolysis of the selenilimines gave only trans selenoxide (**13**) can be explained by the hydration of the cis selenoxide and dehydration to the trans isomer, or by pyramidal inversion of the cis selenoxide to **13**. Ōki and Iwamura reported that benzyl phenyl selenoxide could not be resolved in the optically active form owing to the easy hydration and isomerization of the selenoxide.[9] The trans selenoxide (**13**) did not isomerize at room temperature. Therefore, **13** was heated in acetonitrile for 10 h to give 9-phenylselenoxanthenol (**15**) in 95% yield.

Refluxing **13** in methanol afforded 9-methoxy-9-phenylselenoxanthene (**16**) (58.2%) along with **15** (23.9%), whereas refluxing **13** in toluene yielded bis(9-phenylselenoxanthenyl) ether (**17**) (41.1%) together with **15** (20%).

Trans selenoxide (**13**) caused the syn elimination to form 9-phenylselenoxanthylium ion (**14**) leading to the products **15–17**. From these thermal reactions of **13**, the pathway through hydration and isomerization is preferable to that through pyramidal inversion for the formation of the trans selenoxide (**13**).

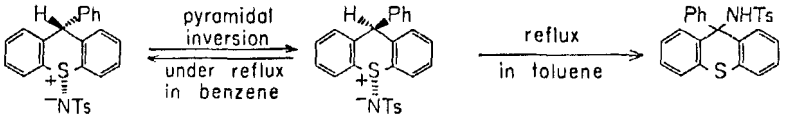
Rearrangements: Next, thermal reactions of the selenilimines were studied. *trans*-9-Phenylselenoxanthene-*N*-(*p*-toluenesulfonyl)selenilimine (*trans*-**10a**) was refluxed in toluene for 6 h to yield the 1,4-rearranged product (**18a**) in 96% yield, whereas *cis*-**10a** neither rearranges to **18a** nor isomerizes to the *trans*-**10a**. The structure of **18a** was determined by the lack of C_9—H in its NMR spectrum. A crossover experiment using *trans*-**10a** and *trans*-9-(pentadeuteriophenyl)selenoxanthene-*N*-(benzenesulfonyl)selenilimine (*trans*-**10c**) was carried out to elucidate the mechanism of the rearrangement. The mass spectrum of the product showed four molecular-ion peaks at m/e 491, 477, 482 and 496 (as Se = 80), which were attributed to the molecular-ion peaks of **18a**, **18b**, **18c** and **18e**, respectively. Production of two crossover products (**18b** and **18e**) showed that this 1,4 rearrangement proceeded intermolecularly via 9-phenylselenoxanthylium ion. The mechanism of the rearrangement of trans selenilimines is outlined in Scheme 6.



SCHEME 6

Trans isomers ring-inverted thermally into another trans conformer D, in which C_9—H and ^-N—R^3 are axial. syn 1,4 Elimination of C_9—H by the N^-—R^3 group generates the selenaanthracene intermediate, which eliminates $^-NHR^3$ to form the selenoxanthylium ion. In the case of cis isomers, neither conformation A nor C in which the relationship between C_9—H and ^-N—R^3 is anti is favorable for such a concerted pathway and the reaction does not proceed. The result described above is markedly different from the fact[6] that refluxing 9-phenylthioxanthene sulfilimine (**19**) in benzene for 10 h produces an equilibrium (cis/trans = ~ 1/3). Tamura and his co-workers discussed the base-catalyzed or acid-catalyzed rearrangements of 9-substituted thioxanthene sulfilimines.[6] However, they did not consider the thermal rearrangement. Therefore, the thermal reaction of **19** (cis/trans = 2/3) was carried out in refluxing toluene for 11 h to give 9-phenyl-9-(*p*-toluenesulfonamido)thioxanthene (**20**) in 70% yield. Since cis and trans thioxanthenesulfilimines isomerize thermally, the cis isomer changes into the trans isomer and an axial ^-N—Ts group abstracts the axial C_9—H by syn elimination to give the thiaanthracene intermediate. The thiaanthracene rearranges intermolecularly to the thioxanthene derivative.

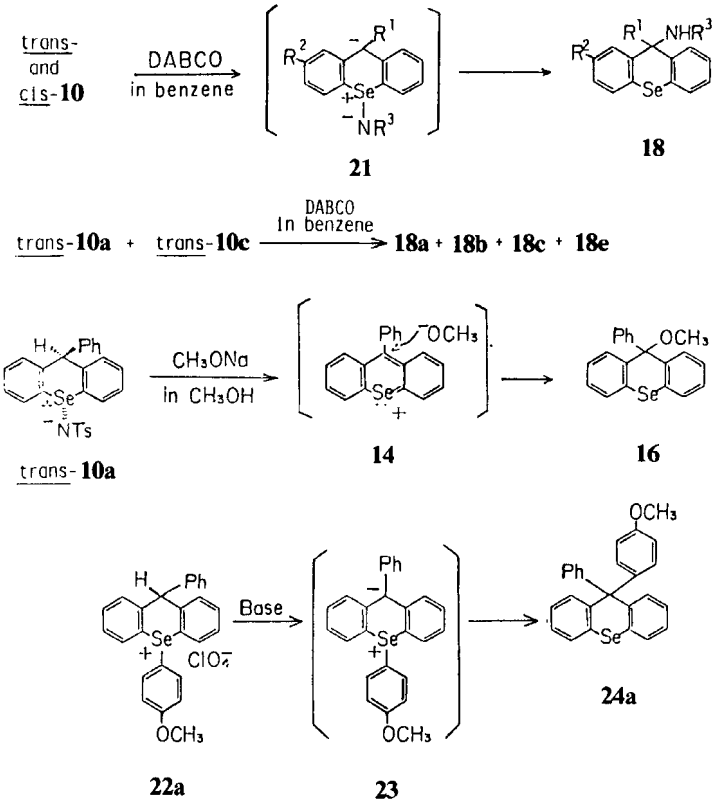
Since cis selenilimine neither isomerizes to the trans isomer nor rearranges to selenoxanthene, pure cis isomer could be isolated from the mixtures of cis and trans isomers by the following method: A mixture of cis and trans isomers (1 : 1) was



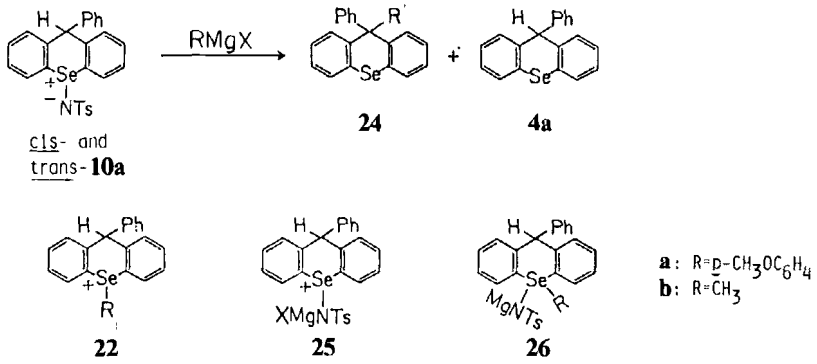
SCHEME 7

heated in refluxing toluene for 6 h. Fractional recrystallization gave the pure *cis*-**10a** and the rearranged product **18a**, which is easier than producing mixtures of cis and trans isomers.

The base-catalyzed reaction of cis selenilimine was examined to determine whether cis selenilimine did not rearrange because of the difficulty of the intramolecular C_9—H abstraction. Reaction of *cis*-**10a** with 1 eq. of 1,4-diazabicyclo[2,2,2]octane (DABCO) in benzene at room temperature yielded the rearranged product, 9-phenyl-9-(*N*-*p*-toluenesulfonamido)selenoxanthene (**18a**) in 95% yield, and *trans*-**10a** rearranged similarly to **18a**. Other selenilimines underwent the 1,4 rearrangement very easily. When sodium methoxide was used in methanol as base, 9-methoxy-9-phenylselenoxanthene (**16**) (80.1%) was obtained. This finding suggested that the base-catalyzed 1,4 rearrangement is an intermolecular reaction. This was confirmed by a crossover experiment of *trans*-**10a** and *trans*-9-pentadeuteriophenyl derivative (*trans*-**10c**) with DABCO which gave the crossover products (**18b** and **18e**). Though the intermediate **21** and 10-(*p*-methoxyphenyl)-9-phenyl-10-selenaantracene (**23**) (the latter is generated from the selenoxanthenium salt (**22a**)) have similar structures, 1,4 rearrangement of **21** differs from the case of the selenaanthracene (**23**) which rearranges intramolecularly to yield 9-(*p*-methoxyphenyl)-9-phenylselenoxanthene (**24a**).[4]

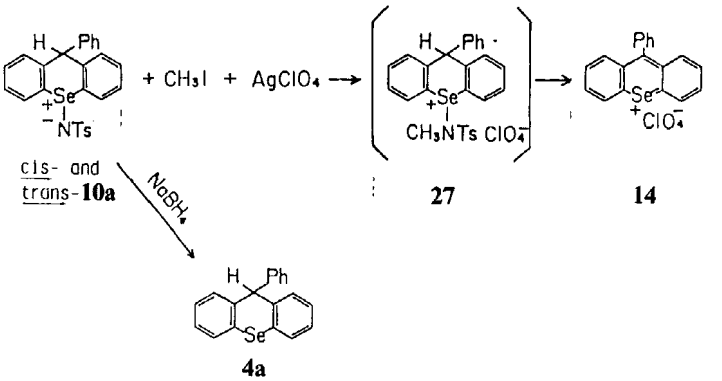


SCHEME 8



SCHEME 9

Grignard Reactions: Selenilimine *trans*-**10a** reacted with 10 eq. of *p*-methoxyphenylmagnesium bromide to give 9-(*p*-methoxyphenyl)-9-phenylselenoxanthene (**24a**) and 9-phenylselenoxanthene (**4a**) in yields of 61.5% and 30.4%, respectively. When a mixture of *trans*- and *cis*-**10a** (1 : 1) was employed, **24a** (57.4%) and **4a** (38.2%) were obtained. On the other hand, reaction of *trans*-**10a** with 10 eq. of methylmagnesium iodide yielded 9-phenylselenoxanthene (**4a**) in 83.3% yield together with 9-methyl-9-phenylselenoxanthene (**24b**) in 7.3% yield. This result is very similar to that of the reaction of 10-methyl-9-phenylselenoxanthenium salt (**22b**) with dimsyl sodium. Consequently, **22b** may be a suitable intermediate for the reaction with methylmagnesium iodide. However, this intermediate cannot be applied to the case of *p*-methoxyphenylmagnesium bromide because the reaction of **22a** with phenyllithium did not yield 9-phenylselenoxanthene.[4] Reactions of 9-phenylselenoxanthylium salt (**14**) with Grignard reagents did not produce **4a**. On the basis of these results, the formation of **4a** would be explained by the way that the nitrogen atom of an intermediate **25** is attacked by R^- or that the σ-selenurane intermediate **26** eliminates the $\begin{matrix} R \\ \diagdown \\ \diagup \\ Ts \end{matrix}$NMgX to form **4a**. Further study will focus on the reaction of selenoxanthenium salts with organometallic reagents to resolve the reaction mechanism of selenilimines with Grignard reagents.



SCHEME 10

Other Reactions: 9-Phenylselenoxanthylium perchlorate (**14**) was obtained in 80.2% yield when a mixture of *trans*- and *cis*-**10a** (1 : 1) was treated with 10 eq. of iodomethane and 1 eq. of silver perchlorate. This reaction might proceed via amidoselenonium salt (**27**), which suffers Se—N bond cleavage to form **14** and *N*-methyltoluenesulfonamide.

Reduction of a mixture of *trans*- and *cis*-**10a** (1 : 1) with sodium borohydride afforded 9-phenylselenoxanthene (**4a**) in 97.9% yield.

EXPERIMENTAL

All melting points were taken on a Yanagimoto micromelting point apparatus and are uncorrected. IR spectra were recorded using a JASCO IRA-1 spectrometer. NMR spectra were measured with a Hitachi R-20B spectrometer using tetramethylsilane as internal standard. Low and high resolution mass spectra were determined with a JEOL JMSD-300 spectrometer and JMA 2000 on-line system at 70 eV.

2-Phenylselenobenzaldehyde (**1**). Sodium benzeneselenolate was prepared from diphenyl diselenide (16.5 g) and sodium borohydride (4.0 g) in ethanol (200 ml) by the method of Sharpless.[10] To the solution was added a solution of 2-chlorobenzaldehyde (13.5 g) in DMF (100 ml). The resulting mixture was heated to 120° and stirred for 4 h at that temperature. The cooled mixture was poured into water and extracted with benzene–hexane (4 : 1). The extracts were washed with water, dried over $MgSO_4$ and concentrated. The residual oil was purified by column chromatography on silica gel using benzene–hexane (1 : 2) as eluent to give **1** (21.6 g, 86.1%). Recrystallization from hexane gave yellow prisms, mp 60–61°. IR (KBr) cm^{-1} 1660 (CHO). NMR ($CDCl_3$) δ 6.90–7.95 (9 H, m, ArH), 10.14 (1 H, s, CHO). MS m/e 262 (M^+, Se = 80). *Anal.* Calcd. for $C_{13}H_{10}OSe$: C, 59.78; H, 3.86. Found: C, 59.51; H, 3.85.

2-(Phenylseleno)phenylphenylmethanol (**3a**). To an ethereal solution of phenylmagnesium bromide prepared from bromobenzene (54 g) and magnesium (8.36 g) was added dropwise an ethereal solution of **1** (30 g) at ice-bath temperature with stirring. After refluxing for 1 h the reaction mixture was decomposed with dil. ammonium chloride and extracted with ether. The extracts were washed with water, dried ($MgSO_4$) and concentrated. The residue was purified by column chromatography on silica gel with benzene to afford **3a** (38.5 g, 98.7%). Recrystallization from dichloromethane–hexane gave colorless needles, mp 66–67°. IR (KBr) cm^{-1} 3440 (OH). NMR ($CDCl_3$) δ 2.50 (1 H, broad s, OH), 6.23 (1 H, s, CHOH), 6.88–7.60 (14 H, m, ArH). MS m/e 340 (M^+, Se = 80). *Anal.* Calcd. for $C_{19}H_{16}OSe$: C, 67.26; H, 4.75. Found: C, 67.33; H, 4.68.

9-Phenylselenoxanthene (**4a**). Compound **3a** (10.0 g) was dissolved in 80 v/v% sulfuric acid (50 ml) and warmed at 95° for 30 min. The cooled mixture was poured on crushed ice and extracted with dichloromethane. The extracts were washed with water, dried ($MgSO_4$) and concentrated. The residue was purified by column chromatography on silica gel using benzene–hexane (1 : 2) as eluent. The first fraction gave **4a** (7.44 g, 79.6%), which was recrystallized from methanol to give colorless plates, mp 115–116° (lit.[4] mp 115°). The second fraction gave bis[2-(diphenylmethyl)phenyl] diselenide (**5a**) (1.02 g, 10.8%), which was recrystallized from chloroform–hexane to give yellow prisms, mp 189–192°. NMR ($CDCl_3$) δ 5.98 (2 H, s, CH), 6.73–7.85 (28 H, m, ArH). MS m/e 646 (M^+, Se = 80). *Anal.* Calcd. for $C_{38}H_{30}Se_2$: C, 70.81; H, 4.69. Found: C, 70.85; H, 4.64.

2-(Phenylseleno)phenylpentadeuteriophenylmethanol (**3b**). In a similar manner as **3a**, **3b** (5.25 g, 99.6%) was obtained from C_6D_5Br (4.964 g), magnesium (0.74 g), and **1** (4.00 g). Compound **3b** was used without further purification. IR (KBr) cm^{-1} 3440 (OH), 2260 (CD). NMR ($CDCl_3$) δ 2.57 (1 H, s, OH), 6.26 (1 H, s, CHOH), 6.90–7.65 (9 H, m, ArH). MS m/e 345 (M^+, Se = 80).

9-Pentadeuteriophenylselenoxanthene (**4b**). In a similar manner as **4a**, **3b** (4.5 g) was cyclized with 80% (v/v) sulfuric acid (25 ml). The raw product was purified by column chromatography to give **4b** (2.95 g, 69.2%) from the first fraction and bis-[2-(pentadeuteriophenyl phenyl methyl)phenyl]diselenide (**5b**) (0.29 g, 6.8%) from the second fraction. The diselenide **5b** was recrystallized from chloroform–hexane to give yellow prisms, mp 188.5–191.5°. IR (KBr) cm^{-1} 2260 (CD). NMR ($CDCl_3$) δ 5.98 (2 H, s, CH), 6.73–7.85 (18 H, m, ArH). MS m/e 656 (M^+, Se = 80). Compound **4b** was identical with the sample[4] by comparison of their mp and IR and NMR spectra.

5-Chloro-2-phenylselenobenzophenone (**2**). To a suspension of diphenyl diselenide (9.32 g) in ethanol (200 ml) was added sodium borohydride (2.27 g) under a nitrogen atmosphere at room temperature. After the mixture became colorless, DMF (100 ml) was added and then ethanol was evaporated off. To the mixture was added dropwise a solution of 2,5-dichlorobenzophenone (15 g) in DMF (70 ml). The resulting mixture was refluxed for 3 h, cooled, poured on crushed ice and extracted with benzene–hexane (4 : 1). The extracts were washed with water, dried over $MgSO_4$ and concentrated. The residual oil was purified by column chromatography on silica gel using ethyl acetate–hexane (1 : 4) as eluent to give **2** (20.8 g, 93.7%) as a yellow oil. Compound **2** was used without further purification. IR (film) cm^{-1} 1660 (CO). NMR ($CDCl_3$) δ 7.0–8.10 (m, ArH). MS m/e 372 (M^+, Se = 80).

(*5-Chloro-2-phenylseleno*)*phenylphenylmethanol* (**3c**). To a solution of **2** (20 g) in methanol (200 ml) was added sodium borohydride (10.2 g) at room temperature, and the mixture was refluxed for 30 min. The cooled mixture was poured into water and extracted with dichloromethane. The extracts were washed with water, dried over $MgSO_4$ and concentrated. The residual oil, **3c** (19.7 g, 98%) was used without further purification. IR (film) cm^{-1} 3370 (OH). NMR ($CDCl_3$) δ 2.72 (1 H, broad s, OH), 6.16 (1 H, s, CH), 6.93–7.73 (13 H, m, ArH). MS m/e 374 (M^+, Se = 80).

2-Chloro-9-phenylselenoxanthene (**4c**). A mixture of **3c** (19.7 g) and 80 v/v% sulfuric acid (50 ml) was warmed at 95–98° for 30 min. The cooled reaction mixture was poured on crushed ice and extracted with dichloromethane. The extracts were washed with water, dried over $MgSO_4$ and concentrated. The residual oil was purified by column chromatography on silica gel using benzene–hexane (1 : 4) as eluent. The first fraction gave **4c** (10.35 g, 55.2%). Recrystallization from methanol gave colorless needles, mp 130–132°. NMR ($CDCl_3$) δ 5.30 (1 H, s, 9 H), 6.77–7.70 (12 H, m, ArH). MS m/e 356 (M^+, Se = 80). *Anal.* Calcd. for $C_{19}H_{13}ClSe$: C, 64.15; H, 3.68. Found: C, 64.40; H, 3.42. The second fraction gave **5c** (800 mg, 4.3%). Recrystallization from hexane gave orange prisms, mp 190–192°. NMR ($CDCl_3$) δ 5.87 (2 H, s, CH), 6.75–7.70 (26 H, m, ArH). MS m/e 714 (M^+, Se = 80). *Anal.* Calcd. for $C_{38}H_{28}Cl_2Se_2$: C, 63.97; H, 3.96. Found: C, 63.98; H, 3.82.

2-(Diphenylmethyl)phenyl Methyl Selenide (**6**). Sodium borohydride (73 mg) was added to a suspension of **5a** (500 mg) in ethanol (10 ml) at room temperature, and the yellow solution turned colorless. To the solution was added iodomethane (2.2 g). After stirring for 30 min, the mixture was poured into water and extracted with ether. The extracts were washed with water, dried over $MgSO_4$ and concentrated. The residual solid was recrystallized from hexane gave **6** (510 mg, 97.5%) as pale yellow prisms, mp 97–99°. NMR ($CDCl_3$) δ 2.22 (3 H, s, CH_3), 6.05 (1 H, s, CH), 6.83–7.60 (14 H, m, ArH). MS m/e 338 (M^+, Se = 80). *Anal.* Calcd. for $C_{20}H_{18}Se$: C, 71.21; H, 5.38. Found: C, 71.36; H, 5.39.

cis- and trans-9-Arylselenoxanthene-N-(arylsulfonyl)selenilimines (**10**). Chloramine T · $3H_2O$ (877 mg) was added to a solution of 9-phenylselenoxanthene (1.00 g) in acetonitrile (100 ml). The mixture was stirred for 3 h at room temperature and concentrated under reduced pressure. To the residue were added water and dichloromethane. The organic layer was separated, dried over $MgSO_4$ and concentrated. The residue was recrystallized from dichloromethane–hexane to afford a mixture of **10** (cis/trans = 1) (1.257 g, 82.3%) as white powders. The mixture was separated by fractional recrystallization from dichloromethane–hexane. Other selenilimines were synthesized similarly. Isomer ratios and yields are shown in Table I, and melting points and spectral data are listed in Table II.

*Reaction of cis-***10b** *with Chloramine-T.* Chloramine T · $3H_2O$ (177 mg) was added to a solution of *cis*-**10b** (300 mg) in acetonitrile (40 ml) at room temperature. The solution was stirred for 3 h and then concentrated under reduced pressure. To the residue were added water and dichloromethane. The organic layer was separated, dried over $MgSO_4$ and concentrated under reduced pressure. The residual oil was crystallized from dichloromethane–hexane to afford a mixture of the selenilimine (180 mg) (*trans*-**10a**/*cis*-**10b** = 5) as white powders.

*Hydrolysis of cis- or trans-***10a**. The selenilimine *cis*-**10a** (100 mg) was placed on silica gel TLC plates and developed using ethyl acetate to afford *p*-toluenesulfonamide (32.8 mg, 94%) and *trans*-9-phenylselenoxanthene 10-oxide (**13**) (63.3 mg, 92%). Recrystallization of **13** from dichloromethane–hexane as colorless prisms, mp 149–152° (dec.). IR (KBr) cm^{-1} 825 (Se—O). NMR ($CDCl_3$) δ 5.58 (1 H, s, 9 H), 6.70–7.05 (2 H, m, $C_{2,6}$—H of C_9—Ph), 7.05–7.80 (9 H, m, ArH), 7.80–8.20 (2 H, m, $C_{4,5}$—H). This compound was identical with the selenoxide[4] obtained by oxidation of **4** with 35% hydrogen peroxide or *m*-chloroperbenzoic acid on the basis of their mp, and IR and NMR spectra.

Thermal Reactions of trans-9-Phenylselenoxanthene 10-Oxide (**13**). (a) A solution of **13** (200 mg) in acetonitrile (4 ml) was refluxed for 10 h, and then concentrated under reduced pressure. The residual oil

was separated by preparative TLC on silica gel using hexane–benzene (1 : 1) as eluent to afford 9-phenylselenoxanthenol (**15**) (190 mg, 95%). Compound **15** was identical with the authentic sample by comparison of mp, and IR and NMR spectra. (b) A suspension of **13** (100 mg) in methanol (10 ml) was refluxed for 30 h, and then concentrated under reduced pressure. The residual oil was separated by preparative TLC on silica gel using hexane–benzene (1 : 1) as eluent. The first fraction gave 9-methoxy-9-phenylselenoxanthene (**16**) (60.6 mg, 58.2%). The compound **16** was identical with the authentic sample[4] by comparison with mp, and IR and NMR spectra. The second fraction gave **15** (23.9 mg, 23.9%). The third fraction gave **13** (9 mg, 9%). (c) A solution of **13** (50 mg) in toluene (5 ml) was refluxed for 3 h and then concentrated under reduced pressure. The residual oil was separated by preparative TLC on silica gel using benzene–hexane (1 : 3). The first fraction gave bis(9-phenylselenoxanthyl)ether (**17**) (20 mg, 41.1%). Recrystallization from benzene–hexane gave colorless prisms, mp 208–210°. NMR ($CDCl_3$) δ 6.35–7.63 (m, ArH). MS m/e 658 (M^+, Se = 80), 337, 321. *Anal.* Calcd. for $C_{38}H_{26}OSe_2$: C, 69.52; H, 3.99. Found: C, 69.53; H, 3.92. The second fraction gave **15** (10 mg, 20%).

*Thermal Rearrangement of trans-***10a**, *trans-***10b** *and trans-***10d**. A suspension of *trans-***10a** (100 mg) in toluene (10 ml) was refluxed for 6 h and concentrated under reduced pressure. The residue was separated by preparative TLC on silica gel using hexane–ethyl acetate (3 : 1) to afford 9-phenyl-9-(*N-p*-toluenesulfonamido)selenoxanthene (**18a**) (98 mg, 98%). In a similar manner as *trans-***10a**, *trans-***10b** (100 mg) and *trans-***10d** (47 mg) yielded 9-(*N*-benzenesulfonamido)-9-phenylselenoxanthene (**18b**) (96 mg, 96%) and 2-chloro-9-(*N*-benzenesulfonamido)-9-phenylselenoxanthene (**18d**) (31 mg, 66%), respectively. These compounds **18a**, **18b** and **18d** were identical with the corresponding compounds obtained by the base-catalyzed rearrangement.

*Crossover Experiment of Thermal Rearrangement of trans-***10a** *and trans-***10c**. A mixture of *trans-***10a** (49 mg) and *trans-***10c** (48.1 mg) in toluene (10 ml) was refluxed for 6 h. Mass spectrum of the reaction mixture showed four molecular ion peaks at m/e 477, 482, 491 and 496, which were attributed to **18b**, **18c**, **18a** and **18e**, respectively. The crossover products **18b** and **18e** were detected, confirming thermal rearrangement proceeded intermolecularly.

Thermal Rearrangement of 9-Phenylthioxanthene-N-(p-toluenesulfonyl)sulfilimine (**19**). A suspension of **19** (30 mg, cis/trans = 2/3) in toluene was refluxed for 11 h and then concentrated under reduced pressure. The residual oil was separated by preparative TLC on silica gel using ethyl acetate–hexane (1 : 3) to afford 9-phenyl-9-(*N-p*-toluenesulfonamido)thioxanthene (**20**) (21 mg, 70%). The compound **20** was identical with the sample reported by Tamura *et al.*[6a]

Base-catalyzed Rearrangement of Selenilimines (**10**). DABCO (22.9 mg) was added to a solution of *trans-***10a** (100 mg) in benzene (10 ml). The mixture was stirred for 24 h at room temperature and then concentrated under reduced pressure. The residue was separated by preparative TLC on silica gel using hexane–ethyl acetate (3 : 1) to afford **18a** (98 mg, 98%). Recrystallization from benzene–hexane gave colorless prisms, mp 211–214° (dec.). IR (KBr) cm^{-1} 3240 (NH), 1330, 1150 (SO_2). NMR ($CDCl_3$) δ 2.34 (3 H, s, CH_3), 5.18 (1 H, s, NH), 6.80–7.50 (17 H, m, ArH). MS m/e 491 (M^+, Se = 80). *Anal.* Calcd. for $C_{26}H_{21}NO_2SSe$: C, 63.67; H, 4.32; N, 2.86. Found: C, 63.90; H, 4.28; N, 2.83. In the similar manners as *trans-***10a**, *cis-***10a** rearranged to **18a** in 94% yield. Other selenilimines rearranged similarly to selenoxanthenes. 9-(*N*-Benzenesulfonamido)-9-phenylselenoxanthene (**18b**) was obtained from *trans-***10b** or *cis-***10b** in the yield of 97% or 95%, respectively. Compound **18b** was recrystallized from benzene–hexane as colorless prisms, mp 213–217° (dec.). IR (KBr) cm^{-1} 3240 (NH), 1335, 1155 (SO_2). NMR ($CDCl_3$) δ 5.16 (1 H, s, NH), 7.00–7.50 (18 H, m, ArH). MS m/e 477 (M^+, Se = 80). *Anal.* Calcd. for $C_{25}H_{19}NO_2SSe$: C, 63.02; H, 4.02; N, 2.94. Found: C, 63.21; H, 3.89; N, 2.78. 2-Chloro-9-(*N*-benzenesulfonamido)-9-phenylselenoxanthene (**18d**) was recrystallized from benzene–hexane as colorless prisms, mp 217–222° (dec.). IR (KBr) cm^{-1} 3230 (NH), 1325, 1155 (SO_2). NMR ($CDCl_3$) δ 5.26 (1 H, s, NH), 6.87–7.50 (1 H, m, ArH). MS m/e 511 (M^+, Se = 80). *Anal.* Calcd. for $C_{25}H_{18}ClNO_2SSe$: C, 58.77; H, 3.55; N, 2.74. Found: C, 58.84; H, 3.38; N, 2.72.

*Crossover Experiment of Base-catalyzed Rearrangement of trans-***10a** *and trans-***10c**. To a solution of *trans-***10a** (49 mg) and *trans-***10c** (48.1 mg) in benzene (10 ml) was added DABCO (22.5 mg), and the mixture was stirred for 24 h at room temperature. Mass spectrum of the reaction mixture showed four molecular ion peaks at m/e 477, 482, 491 and 496 which corresponded to **18b**, **18c**, **18a** and **18e**, respectively. Two crossover products **18b** and **18e** were detected.

Reaction of **10a** *with Sodium Methoxide*. A mixture of *cis-* and *trans-***10a** (1 : 1) was added to a solution of 0.46 *N* sodium methoxide in methanol (10 ml). After stirring for 30 min at room temperature, the reaction mixture was poured into water and extracted with dichloromethane. The extracts were washed with water,

dried over $MgSO_4$, and concentrated. The residue was purified by preparative TLC on silica gel using benzene–hexane (1 : 1) to give **16** (28.1 mg, 80.1%).

Reaction of **10a** *with p-Methoxyphenylmagnesium Bromide.* (a) To an ethereal solution of *p*-methoxyphenylmagnesium bromide prepared from *p*-bromoanisole (1.907 g), magnesium (248 mg) in dry ether (30 ml), a solution of *trans*-**10a** (500 mg) in dry benzene (40 ml) was added dropwise at room temperature under a nitrogen atmosphere. After refluxing for 3 h, the reaction mixture was decomposed with dil. ammonium chloride. The organic layer was separated, washed with water, dried over $MgSO_4$. Removal of the solvent gave a residue, which was purified by column chromatography on silica gel using benzene–hexane as eluent. The first fraction gave **4a** (99.5 mg, 30.4%). The second fraction gave 9-(*p*-methoxyphenyl)-9-phenylselenoxanthene (**24a**) (268 mg, 61.5%). (b) In a similar manner as *trans*-**10a**, a mixture of *trans*- and *cis*-**10a** (1 : 1) (500 mg) afforded **4a** (125 mg, 38.2%) and **24a** (250 mg, 57.4%).

Reaction of trans-**10a** *with Methylmagnesium Iodide.* To an ethereal solution of methylmagnesium iodide prepared from iodomethane (1.45 g) and magnesium (248 mg) in ether (30 ml) was added dropwise a solution of *trans*-**10a** (500 mg) in benzene (40 ml) at room temperature. After refluxing for 3 h, the reaction mixture was decomposed with dil. ammonium chloride. The organic layer was separated, washed with ether and dried over $MgSO_4$. Removal of the solvent afforded a residue, which was separated by preparative TLC on silica gel using ethyl acetate–hexane (1 : 30). The less polar fraction gave 9-methyl-9-phenylselenoxanthene (**24b**) (25 mg, 7.3%) and the more polar fraction afforded **4a** (274 mg, 83.8%). These compounds were identical with the authentic sample by comparison of their mp, and IR and NMR spectra.

Reaction of **10a** *with Iodomethane and Silver Perchlorate.* To a solution of a mixture of *trans*- and *cis*-**10a** (1 : 1) and iodomethane (1.42 g) in dichloromethane (10 ml) was added silver perchlorate (90% pure) (230 mg). The mixture was stirred for 36 h at room temperature. The precipitate was filtered off and the filtrate was concentrated to dryness. The residue was treated with ether and benzene to afford 9-phenylselenoxanthylium perchlorate (**14**) (336 mg, 80.2%) as purple powders.

Reduction of **10a** *with Sodium Borohydride.* (a) Sodium borohydride (39 mg) was added to a solution of *trans*-**10a** (50 mg) in a mixture of ethanol (5 ml) and dichloromethane (2.5 ml) at room temperature. After stirring for 30 min, the mixture was poured into water and extracted with dichloromethane. The extracts were washed with water, dried over $MgSO_4$ and concentrated. The residue was separated by preparative TLC on silica gel using benzene–hexane (1 : 3) to afford **4a** (28 mg, 85.5%). (b) In a similar manner as *trans*-**10a**, a mixture of *trans*- and *cis*-**10a** (1 : 1) (50 mg) gave **4a** (32 mg, 97.9%).

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