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Synthesis, Stereochemistry and Reactions of Selenoxanthen-10-io(alkoxalyl alkoxycarbonyl)methanides and Related Compounds[1]

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Selenoxanthene 10-oxides (**5a**—**d**) reacted with methyl propiolate, dimethyl and diethyl acetylenedicarboxylates to afford selenoxanthen-10-io[formyl (or alkoxalyl) alkoxycarbonyl]-methanides (**6a**—**i**). The 9-isopropyl derivative gave only *trans*-ylides and the 9-phenyl congener formed *cis*- and *trans*-ylides. The stereochemistry is discussed on the basis of the nuclear magnetic resonance spectral data.

Reduction of the selenoxanthenium ylides with sodium borohydride afforded the ylide lactones (**16a**—**c**) and the ylide alcohols (**17a**—**f**). The product ratio depended on the solvent used.

Keywords——selenium ylide; selenoxide; selenoxanthene; methyl propiolate; dimethyl acetylenedicarboxylate; diethyl acetylenedicarboxylate; stereoisomer; stereochemistry; sodium borohydride reduction; lactonization

Recently the synthesis of stable selenium ylides has been reported. However, the stereochemistry of the selenium ylides has been little studied. Sakaki and Oae reported on the asymmetric synthesis of optically active selenium ylides,[2a] and a few ylides of selenium heterocycles have been prepared.[2b,c] X-Ray analysis of an ylide showed that the configuration at selenium was pyramidal.[2d]

We selected the selenium heterocycles for stereochemical studies of the hypervalent selenium atom. We previously reported on the synthesis, stereochemistry, and stereospecific reactions of *cis*- and *trans*-9-phenylselenoxanthene-*N*-(arylsulfonyl)selenilimines.[3] This paper deals with the synthesis, stereochemistry and reactions of 9-substituted selenoxanthen-10-io(alkoxalyl alkoxycarbonyl)methanides, which are isoelectronic to the selenilimines.

Synthesis

2-Phenylselenobenzaldehyde (**1**) was treated with 80 v/v% sulfuric acid and then with water to afford selenoxanthene (**2**) and selenoxanthone (**3**) in 46.2 and 49.1% yields, respectively. The formation of **2** and **3** may be explained in terms of a process involving an intermolecular hydride shift from selenoxanthenol to the selenoxanthylium cation.[4] 9-Isopropylselenoxanthene (**4**) was prepared from **2** by deprotonation with *n*-butyllithium followed by reaction with isopropyl iodide. Selenoxanthenes (**2**, **4**) were oxidized with *m*-chloroperbenzoic acid (MCPBA) to give selenoxanthene 10-oxides (**5a**, **b**) in 92.0 and 97.6% yields, respectively. The selenoxide (**5b**) was obtained as a single isomer. The stereostructure of the selenoxide (**5b**) was ascertained by ASIS (aromatic solvent-induced shift) studies and by comparison of the nuclear magnetic resonance (NMR) spectra with those of the corresponding sulfoxides.[5] The chemical shifts of C_9–H (δ 3.75) and the 9-isopropyl group [δ 0.87 (CH_3) and 1.05—1.95 (CH)] of **5b** are closer to those of the *trans*-isomer of the corresponding sulfoxide than to those of the *cis*-isomer.[5b] If the seleninyl group were in the pseudoaxial position, the signal of a pseudoaxial C_9–H would be shifted greatly downfield. Such a shift was not apparent in the NMR spectrum of **5b**. These observations define not only the *trans*-

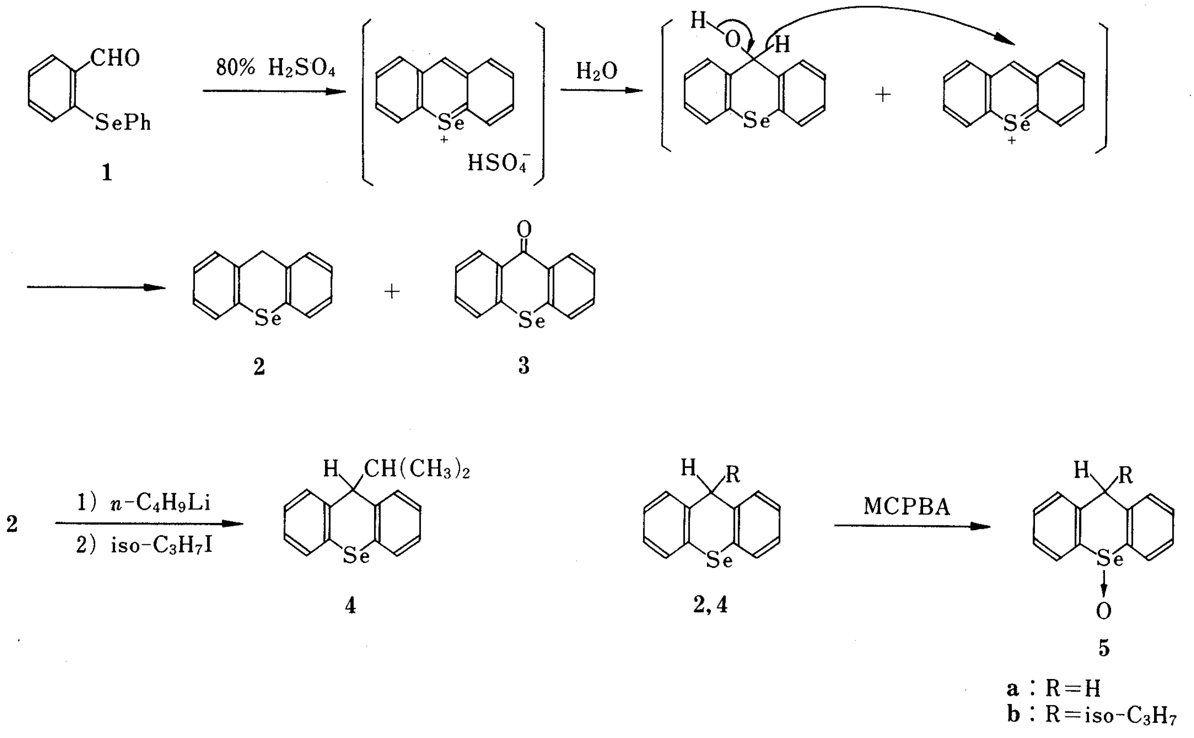
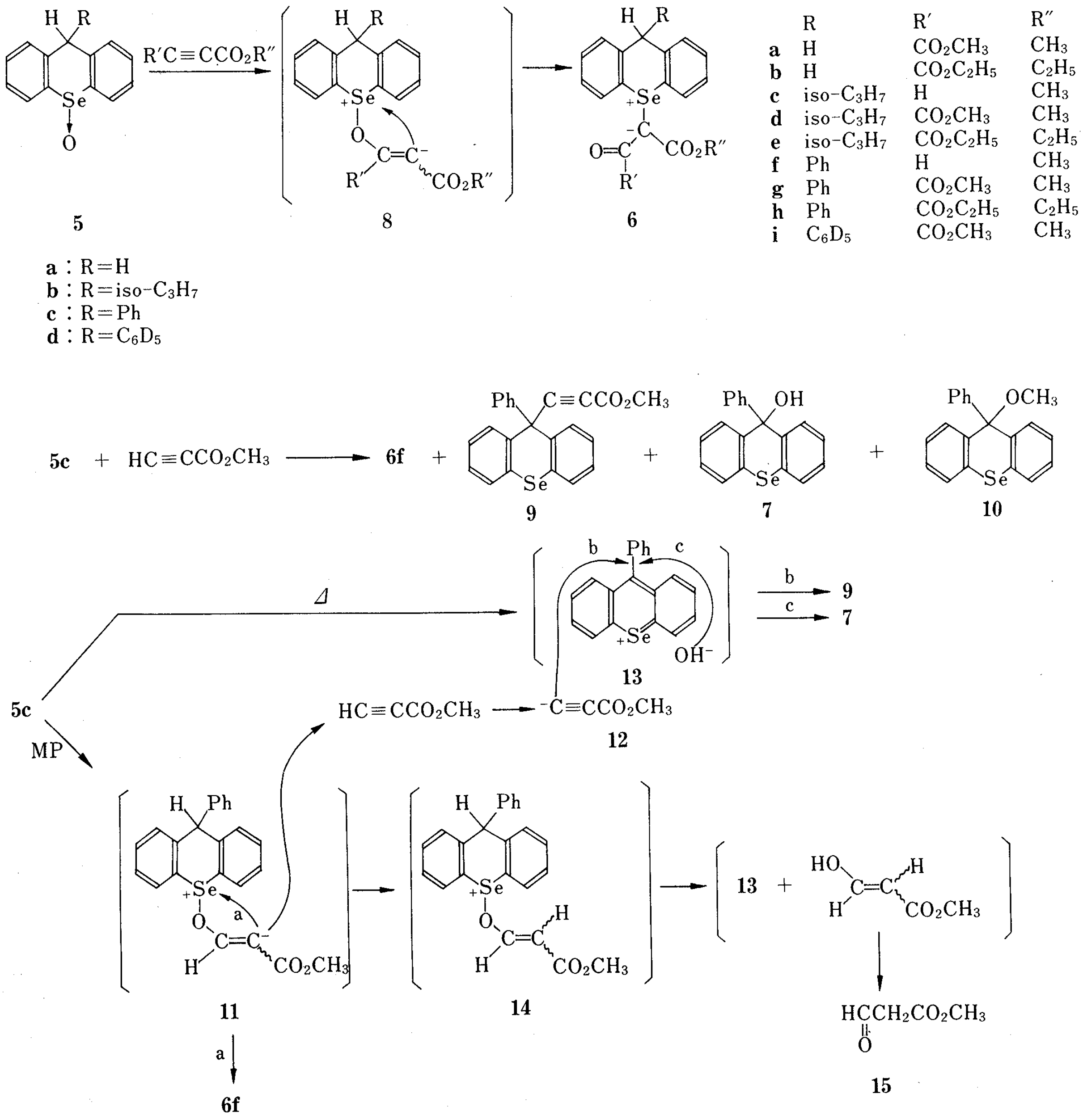


Chart 1

stereochemistry of **5b** but also the pseudoequatorial conformation of the seleninyl group. Selenoxanthene 10-oxides possessing a pseudoequatorial seleninyl group showed negative ASIS values[6] (−0.09 for **5b**—**d**).

It is known that the reactions of selenoxides and electron-deficient acetylenic compounds give selenium ylides.[2c,7] However, no report has been published on the reactions of diaryl selenoxides with the acetylenic compounds. Selenoxanthene 10-oxides (**5a**—**d**) reacted with acetylenic compounds such as methyl propiolate (MP), dimethyl acetylenedicarboxylate (DMAD) and diethyl acetylenedicarboxylate (DEAD) to form selenoxanthen-10-io[formyl (or alkoxalyl) alkoxycarbonyl]methanides (**6a**—**i**). The reaction conditions and yields are shown in Table I. The thermal stability of the selenoxides and the reactivity of the acetylenes affected the yields of these reactions. The selenoxides (**5b**—**d**) were fairly stable in dichloromethane at room temperature, but **5a** gradually decomposed to selenoxanthene (**2**) and selenoxanthone (**3**). Compound **5b** was stable in refluxing acetonitrile, but **5c** afforded 9-phenylselenoxanthenol (**7**).[3] *cis*- and *trans*-ylides (**6f**—**i**) were obtained from the *trans*-selenoxides (**5c**—**d**).[3] The formation of **6** can be explained by a pathway through a betaine intermediate (**8**). DMAD or DEAD is attacked by seleninyl oxygen to form the betaine (**8**), whose carbanion can attack the selenium atom, then Se–C bond formation and Se–O bond fission lead **8** to the ylide (**6**). At present, we have no evidence regarding the detailed mechanism of *trans*-formation of the betaine (**8**) to the ylide (**6**).

Refluxing of **5c** with 10 eq of MP in dichloromethane afforded **6f** (26.9%), **7** (26.3%), methyl 9-phenylselenoxanthen-9-ylpropiolate (**9**) (22.0%) and 9-methoxy-9-phenylselenoxanthene (**10**) (7.9%). The structure of **9** was determined by the spectral evidence: the infrared (IR) spectrum showed absorptions of an acetylenic bond at 2235 cm^{-1} and an ester carbonyl group at 1715 cm^{-1}; the ^{1}H-NMR spectrum had no signal due to C_9–H; the mass spectrum ($M^+ = 404$, Se = 80) and elemental analysis gave a molecular formula of $C_{23}H_{16}O_2Se$. One possible reaction mechanism is shown in Chart 2: the betaine (**11**) abstracts the acetylenic proton of MP to form the ethynyl carbanion (**12**) and a selenonium ion (**14**),



	R	R′	R″
a	H	CO_2CH_3	CH_3
b	H	$CO_2C_2H_5$	C_2H_5
c	iso-C_3H_7	H	CH_3
d	iso-C_3H_7	CO_2CH_3	CH_3
e	iso-C_3H_7	$CO_2C_2H_5$	C_2H_5
f	Ph	H	CH_3
g	Ph	CO_2CH_3	CH_3
h	Ph	$CO_2C_2H_5$	C_2H_5
i	C_6D_5	CO_2CH_3	CH_3

a : R=H
b : R=iso-C_3H_7
c : R=Ph
d : R=C_6D_5

Chart 2

and the carbanion (**12**) attacks the 9-phenylselenoxanthylium cation (**13**) formed by the thermal reaction[3] of **5c** to give **9**. 9-Methoxy-9-phenylselenoxanthene (**10**) would be formed by the reaction of **13** and methanol contained in dichloromethane as a stabilizer. Attempts to detect methyl formylacetate (**15**) were unsuccessful.[8]

Stereochemistry

Stereoisomers of selenoxanthenium ylides can exist in four conformational isomers (A—D) as shown in Chart 3. There has been no report concerning the stereochemistry of selenoxanthenium ylides. We determined the stereochemistry of the selenium ylides (**6a**—**i**) on the basis of the results obtained with thioxanthenium ylides[9,10] and selenoxanthene selenilimines.[3] Ternay *et al.* reported that the bisalkoxycarbonyl methanide groups of thioxantheniomethanides lacking substituents at C_4 exist preferentially in the pseudoequatorial conformation.[10c] Since the selenoxantheniomethanides under discussion have no 4-methyl group, the alkoxalyl (or formyl) alkoxycarbonylmethanide group (an X group in Chart 3)

TABLE I. Syntheses of Selenoxantheniomethanides (**6a**—**i**)

Compd.	Acetylene (molar ratio)	Solvent	Time (h)	Temperature	Isolation method[a]	Product (% yield[b]; ratio of *cis* : *trans*)
5a	DMAD (2)	CH_2Cl_2	40	r.t.	A	**6a** (51.2)
5a	DMAD (5)	CH_2Cl_2	4	r.t.	A	**6a** (56.2)
5a	DEAD (2)	CH_2Cl_2	16 2	r.t. and then Reflux	B	**6b** (72.8)
5b	MP (2)	CH_3CN	65	Reflux	C	*trans*-**6c** (52.5)[c]
5b	DMAD (2)	$CHCl_3$	22	Reflux	C	*trans*-**6d** (72.8)[c]
5b	DEAD (2)	$CHCl_3$	24	Reflux	C	*trans*-**6e** (60.7)[c]
5c	MP (2)	CH_3CN	12	Reflux	D	**6f** (13.1; 1 : 6), **7** (75.2)
5c	MP (3.7)	CH_2Cl_2	82 62	r.t. and then Reflux	D	**6f** (38.3; 1 : 10.7)
5c	MP (10)	CH_2Cl_2	72	Reflux	C	**6f** (26.9; 1 : 9.3)
5c	DMAD (1)	DMF	67	r.t.	D	**6g** (47.5; 1 : 6.7)
5c	DMAD (1)	CH_3CN	140	r.t.	D	**6g** (57.7; 1 : 3.7)
5c	DEAD (1)	CH_3CN	312	r.t.	C	*trans*-**6h** (71.3)[c]
5c	DEAD (2)	CH_2Cl_2	15 8.5	r.t. and then Reflux	C	*trans*-**6h** (49.2)[c]
5d	DMAD (1)	CH_3CN	156	r.t.	D	**6i** (77.7; 1 : 6.6)
5d	DMAD (5)	$CHCl_3$	16	r.t.	D	**6i** (40.2; 1 : 10)

a) A, crystallization from dichloromethane–ether–hexane; B, recrystallization from benzene–hexane; C, column chromatography using benzene–ethyl acetate (1 : 1); D, thin-layer chromatography using benzene–ethyl acetate (1 : 1).
b) Isolated yield.
c) *cis*-Isomer could not be isolated.
r.t.: room temperature.

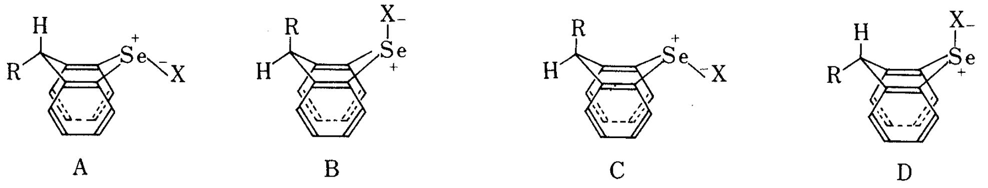


Chart 3

would be pseudoequatorial. If the X group were in the pseudoaxial position, the chemical shift of a pseudoaxial C_9–H or substituent would be greatly affected by the anisotropy of the methanide group. Such an anisotropic deshielding shift was not apparent in the NMR spectra of **6a**—**i**. Therefore the preferred structures of the selenoxantheniomethanides are structures A and C in Chart 3.

The two C_9–H signals of **6a** appear at δ 3.97 and 4.35 as an AB quartet (J = 16.8 Hz). The doublet of δ 3.97 is slightly broadened due to allylic coupling with the *peri*-hydrogens ($C_{1,8}$–H). Compound **6b** exhibited similar absorptions due to C_9–H. The upper doublet of δ 3.97 was assigned to pseudoaxial C_9–H. The chemical shifts of C_9–H of the ylides (**6c**—**e**) are very close to those of pseudoequatorial C_9–H of the selenoxide (**5b**). Therefore, C_9–H and the isopropyl group of the ylides (**6c**—**e**) occupy pseudoequatorial and pseudoaxial conformations, respectively, and the selenium ylides (**6c**—**e**) have the *trans* configuration.

The C_9–H signals of two isomers of **6g** appeared at δ 5.04 and 5.67. The signal at δ 5.04 is shielded by the selenoxanthene ring, and C_9–H occupies the pseudoaxial position. The isomer exhibiting the C_9–H signal at δ 5.04 is the *cis*-isomer and the other having the C_9–H signal at δ 5.67 is the *trans*-isomer. On the other hand, conformations of the 9-phenyl group were confirmed by comparison of the 9-phenyl signals of **6g** with those of the 9-penta-

TABLE II. IR and NMR Data for Selenoxantheniomethanides (**6a**—**i**)

Compd.	IR $\nu_{C=O}$ (cm^{-1})	NMR ($CDCl_3$) (δ)
6a	1585, 1660 1730	3.47 (3H, s, CO_2CH_3), 3.86 (3H, s, CO_2CH_3), 3.97 (1H, d, $J=16.8$ Hz, C_9–H), 4.35 (1H, d, $J=16.8$ Hz, C_9–H), 7.25—7.80 (8H, m, ArH)
6b	1585, 1670 1725	0.72 (3H, t, $J=7.2$ Hz, $CO_2CH_2\underline{CH_3}$), 1.40 (3H, t, $J=7.2$ Hz, $CO_2CH_2\underline{CH_3}$), 3.84 (2H, q, $J=7.2$ Hz, $CO_2\underline{CH_2}CH_3$), 4.00 (1H, d, $J=16.8$ Hz, C_9–H), 4.36 (1H, d, $J=16.8$ Hz, C_9–H), 4.38 (2H, q, $J=7.2$ Hz, $CO_2\underline{CH_2}CH_3$), 7.25—7.85 (8H, m, ArH)
trans-**6c**	1595, 1665	0.85 [6H, d, $J=6.0$ Hz, $CH(\underline{CH_3})_2$], 1.50—2.30 [1H, m, $C\underline{H}(CH_3)_2$], 3.00—4.25 (3H, br, CO_2CH_3), 3.89 (1H, d, $J=10.2$ Hz, C_9–H), 7.25—7.85 (8H, m, ArH), 9.60—10.00 (1H, br s, CHO)
trans-**6d**	1560, 1645 1740	0.86 [6H, d, $J=6.0$ Hz, $CH(\underline{CH_3})_2$], 1.45—2.25 [1H, m, $C\underline{H}(CH_3)_2$], 2.90—4.10 (3H, br, CO_2CH_3), 3.84 (1H, d, $J=9.6$ Hz, C_9–H), 3.89 (3H, s, CO_2CH_3), 7.30—7.90 (8H, m, ArH)
trans-**6e**	1575, 1650 1725	−0.05—1.70 (3H, br, $CO_2CH_2\underline{CH_3}$), 0.86 [6H, d, $J=6.0$ Hz, $CH(\underline{CH_3})_2$], 1.43 (3H, t, $J=7.2$ Hz, $CO_2CH_2\underline{CH_3}$), 1.45—2.25 [1H, m, $C\underline{H}(CH_3)_2$], 3.25—4.70 (2H, br, $CO_2\underline{CH_2}CH_3$), 3.87 (1H, d, $J=10.2$ Hz, C_9–H), 4.44 (2H, q, $J=7.2$ Hz, $CO_2\underline{CH_2}CH_3$), 7.30—7.90 (8H, m, ArH)
cis-**6f**	1600, 1690	3.67 (3H, s, CO_2CH_3), 5.00 (1H, s, C_9–H), 7.00—7.85 (13H, m, ArH), 9.71 (1H, s, CHO)
trans-**6f**	1585, 1600 1675	3.52 (3H, s, CO_2CH_3), 5.65 (1H, s, C_9–H), 6.60—7.00 (2H, m, $C_{2',6'}$–H), 7.00—7.85 (11H, m, ArH), 9.68 (1H, s, CHO)
cis-**6g**	1580, 1675 1740	3.55 (3H, s, CO_2CH_3), 3.90 (3H, s, CO_2CH_3), 5.04 (1H, s, C_9–H), 7.00—7.90 (13H, m, ArH)
trans-**6g**	1585, 1665 1740	3.42 (3H, s, CO_2CH_3), 3.86 (3H, s, CO_2CH_3), 5.67 (1H, s, C_9–H), 6.60—7.00 (2H, m, $C_{2',6'}$–H), 7.00—7.95 (11H, m, ArH)
trans-**6h**	1560, 1655 1740	0.61 (3H, t, $J=7.2$ Hz, $CO_2CH_2\underline{CH_3}$), 1.39 (3H, t, $J=7.2$ Hz, $CO_2CH_2\underline{CH_3}$), 3.74 (2H, q, $J=7.2$ Hz, $CO_2\underline{CH_2}CH_3$), 4.37 (2H, q, $J=7.2$ Hz, $CO_2\underline{CH_2}CH_3$), 5.67 (1H, s, C_9–H), 6.60—7.00 (2H, m, $C_{2',6'}$–H), 7.00—7.90 (11H, m, ArH)
cis-**6i**	1580, 1675 1740, 2260[a]	3.55 (3H, s, CO_2CH_3), 3.90 (3H, s, CO_2CH_3), 5.04 (1H, s, C_9–H), 7.00—7.90 (8H, m, ArH)
trans-**6i**	1585, 1665 1740, 2270[a]	3.42 (3H, s, CO_2CH_3), 3.86 (3H, s, CO_2CH_3), 5.67 (1H, s, C_9–H), 7.35—7.90 (8H, m, ArH)

a) ν_{C-D}.

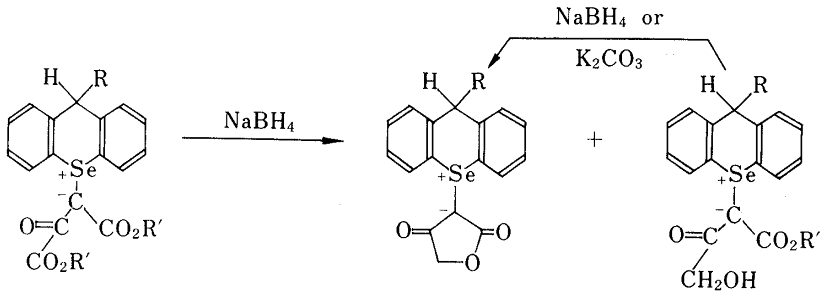
deuteriophenyl derivative (**6i**). The *trans*-isomer (*trans*-**6g**) showed an upfield-shifted multiplet at δ 6.60—7.00 due to $C_{2,6}$–H of the 9-phenyl group and *cis*-**6g** exhibited a multiplet at δ 7.00—7.25 due to $C_{1,8}$–H. The former is shielded by the selenoxanthene ring and the latter is shielded by the 9-phenyl group. Therefore, the 9-phenyl group of *trans*-**6g** is in the pseudoaxial position and that of *cis*-**6g** is in the pseudoequatorial position. Other ylides (**6f**, **h**, **i**) showed similar behavior.

Consequently the *cis* and *trans* isomers of the ylides discussed here are conformers A and C, respectively.

In the NMR spectra of the ylides (**6**), the signals of the two alkoxy groups of 9-isopropylselenoxantheniomethanides (**6c**—**e**) showed broad or split signals, whereas those of other congeners (**6a**, **b**, **f**—**i**) showed sharp signals. This indicates that the rotation about the alkoxy groups is free in the latter ylides and hindered in the former ylides. Similar phenomena have been observed in some thioxantheniomethanides.[9,10d)]

Reactions with Sodium Borohydride

Previously we reported that the reaction of selenoxanthene selenilimines with sodium borohydride gave selenoxanthene in good yields.[3)] Ternay *et al.* prepared 9-hydroxy-



6 16 17

a : R=H
b : R=iso-C_3H_7
c : R=Ph

a : R=H, R′=CH_3
b : R=H, R′=C_2H_5
c : R=iso-C_3H_7, R′=CH_3
d : R=iso-C_3H_7, R′=C_2H_5
e : R=Ph, R′=CH_3
f : R=Ph, R′=C_2H_5

Chart 4

Table III. Reactions of Selenoxantheniomethanides with Sodium Borohydride

Compd.	$NaBH_4$ (molar ratio)	Solvent ($EtOH:CH_2Cl_2$)	Time (h)	Isolation method[b]	Product (% yield)
6a	2	1:10	20	A	**16a** (trace), **17a** (69.9)
6a	2	10: 1	48	B	**16a** (56.8)
6a	10	10: 1	8	B	**16a** (80.4), **17a** (trace)
6b	10	1:10	7	C	**16a** (trace), **17b** (75.2)
6b	10	EtOH[a]	0.5	B	**16a** (67.3)
6b	0.5	10: 1	144	F	**16a** (24.7), **17b** (trace)[c]
trans-**6c**	2	1:10	9	B	[d]
trans-**6d**	2	1:10	3	A	*trans*-**16b** (trace), *trans*-**17c** (64.5)
trans-**6d**	10	EtOH	2	D	*trans*-**16b** (72.2)
trans-**6e**	2	1:10	2.5	A	*trans*-**16b** (trace), *trans*-**17d** (63.6)
trans-**6e**	10	EtOH	3	D	*trans*-**16b** (63.9)
trans-**6g**	2	1:10	3	E	*trans*-**16c** (trace), *trans*-**17e** (71.2)
trans-**6g**	10	2: 1	9	B	*trans*-**16c** (65.1)
trans-**6h**	2	1:10	12	A and F	*trans*-**16c** (4.8), *trans*-**17f** (72.8)
trans-**6h**	10	2: 1	24	B	*trans*-**16c** (56.9)

a) This reaction was carried out under reflux, while the other reactions were conducted at room temperature.
b) A: column chromatography using ethyl acetate. B: crystallization from dichloromethane–ether. C: recrystallization from ethyl acetate–hexane. D: recrystallization from dichloromethane–hexane. E: column chromatography using ethyl acetate–benzene (1 : 1). F: column chromatography using acetone.
c) **6b** was recovered in 28% yield.
d) *trans*-**6c** was recovered in 87.5% yield.

thioxanthen-10-iobis(methoxycarbonyl)methanides by the reduction of the corresponding ketones.[10d] Since the ylides reported here are rather stable and have three carbonyl groups with different properties, we expected that the carbonyl groups could be interconverted into other functional groups without Se–C bond fission by reduction with sodium borohydride.

Reduction of the selenium ylide (**6b**) with 10 eq of sodium borohydride in refluxing ethanol afforded a new ylide, 3-(selenoxanthen-10-io)-2,4-dioxooxolan-3-ide (**16a**) in 67.3% yield, whereas reduction of **6b** in ethanol–dichloromethane (1 : 10) at room temperature gave an ylide alcohol, (selenoxanthen-10-io)-1-hydroxyacetyl-1-ethoxycarbonylmethanide (**17b**), in 75.2% yield along with a trace amount of the lactone (**16a**). The structures of the lactones (**16a**—**c**) were determined by consideration of the spectral data. The IR spectra of the lactones

TABLE IV. IR and NMR Data for 3-(Selenoxanthen-10-io)-2,4-dioxooxolan-3-ides (**16a**—**c**) and Selenoxanthen-10-io(hydroxyacetyl ethoxycarbonyl)methanides (**17a**—**f**)

Compd.	IR $\nu_{\max}^{\text{KBr}}$ (cm^{-1})	NMR ($CDCl_3$) (δ)
16a	1635, 1725	4.01 (1H, d, J=16.8 Hz, C_9–H), 4.51 (1H, d, J=16.8 Hz, C_9–H), 4.54 (2H, s, $COCH_2O$), 7.20—7.80 (8H, m, ArH)
trans-**16b**	1630, 1720	0.90 [6H, d, J=6.3 Hz, $CH(\underline{CH_3})_2$], 1.35—2.25 [1H, m, $C\underline{H}(CH_3)_2$], 3.95 (1H, d, J=10.2 Hz, C_9–H), 4.71 (2H, s, $COCH_2O$), 7.25—7.85 (8H, m, ArH)
trans-**16c**	1635, 1725	4.63 (2H, s, CH_2), 5.71 (1H, s, C_9–H), 6.60—7.00 (2H, m, $C_{2',6'}$–H), 7.00—8.00 (11H, m, ArH)
17a	1595, 1665 3360	3.44 (3H, s, CO_2CH_3), 3.94 (1H, br t, J=3.6 Hz, $CH_2O\underline{H}$), 3.99 (1H, d, J=16.8 Hz, C_9–H), 4.31 (1H, d, J=16.8 Hz, C_9–H), 4.72 (2H, d, J=3.6 Hz, $\underline{CH_2}OH$), 7.20—7.75 (8H, m, ArH)
17b	1590, 1655 3370	0.60 (3H, t, J=7.2 Hz, $CO_2CH_2\underline{CH_3}$), 3.72 (2H, q, J=7.2 Hz, $CO_2\underline{CH_2}CH_3$), 3.96 (1H, d, J=16.8 Hz, C_9–H), 4.05 (1H, t, J=4.5 Hz, $CH_2O\underline{H}$), 4.27 (1H, d, J=16.8 Hz, C_9–H), 4.74 (2H, d, J=4.5 Hz, $\underline{CH_2}OH$), 7.25—7.72 (8H, m, ArH)
trans-**17c**	1585, 1660 3380	0.86 [6H, d, J=6.3 Hz, $CH(\underline{CH_3})_2$], 1.45—2.25 [1H, m, $CH(CH_3)_2$], 2.94, 3.87 (3H, br, CH_3), 3.88 (1H, d, J=10.2 Hz, C_9–H), 4.37 (1H, br s, $CH_2O\underline{H}$), 4.74 (2H, br s, $\underline{CH_2}OH$), 7.25—7.75 (8H, m, ArH)
trans-**17d**	1570, 1665 3400	−0.15—1.65 (3H, br, $CO_2CH_2\underline{CH_3}$), 0.88 [6H, d, J=6.3 Hz, $CH(CH_3)_2$], 1.45—2.25 [1H, m, $C\underline{H}(CH_3)_2$], 3.15—4.95 (2H, br, $CO_2\underline{CH_2}CH_3$), 3.89 (1H, d, J=10.2 Hz, C_9–H), 4.15—4.35 (1H, br, $CH_2O\underline{H}$), 4.75—5.00 (2H, br, $\underline{CH_2}OH$), 7.25—7.80 (8H, m, ArH)
trans-**17e**	1580, 1655 3390	3.44 (3H, s, CO_2CH_3), 3.96 (1H, t, J=4.5 Hz, $CH_2O\underline{H}$), 4.76 (2H, d, J=4.5 Hz, $\underline{CH_2}OH$), 5.75 (1H, s, C_9–H), 6.70—7.10 (2H, m, $C_{2',6'}$–H), 7.10—7.95 (11H, m, ArH)
trans-**17f**	1585, 1650 3340	0.51 (3H, t, J=7.2 Hz, $CO_2CH_2\underline{CH_3}$), 3.68 (2H, q, J=7.2 Hz, $CO_2\underline{CH_2}CH_3$), 3.90—4.20 (1H, $CH_2O\underline{H}$), 4.80 (2H, s, $\underline{CH_2}OH$), 5.73 (1H, s, C_9–H), 6.70—7.10 (2H, m, $C_{2',6'}$–H), 7.10—7.45 (3H, m, $C_{3',4',5'}$–H), 7.45—8.00 (8H, m, ArH)

(**16**) showed five-membered lactone absorptions at 1720—1725 cm^{-1}. Such lowering of the frequency is good evidence for delocalization of the ylidic carbanion. The alcohol (**17b**) was easily converted into the lactone (**16a**) by reduction (sodium borohydride in ethanol), or by treatment with potassium carbonate in a mixture of ethanol–dichloromethane–water. The alcohol (**17b**) was not obtained but only the lactone (**16a**) was formed, even when 0.5 eq of sodium borohydride was used in ethanol–dichloromethane (10 : 1). Other ylides were also reduced by sodium borohydride under the conditions shown in Table III.

The ylidic carbanion is stabilized by a keto group and an ester carbonyl group adjacent to the carbanionic carbon. This is demonstrated by the result that the carbonyl stretching frequencies of the keto and the ester groups fall in the ranges of 1560—1600 and 1645—1690 cm^{-1}, respectively. Therefore, these carbonyl groups could not be reduced with sodium borohydride. Furthermore, **6c** (without the ester adjacent to the ketone) was fairly stable under the reductive conditions used for **6d** and did not give the alcohol.

Further reactions of the selenoxantheniomethanides are under investigation.

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. NMR spectra were measured on a Hitachi R-24 spectrometer with tetramethylsilane as an internal standard. Mass spectra (MS) were recorded on a JEOL JMS-D-300 spectrometer and high resolution MS were taken on a JMA-2000 on-line system.

Cyclization of 2-Phenylselenobenzaldehyde (1)——2-Phenylselenobenzaldehyde (1)[3] (10.0 g, 38.3 mmol) was dissolved in 80 v/v% sulfuric acid (100 ml) and the solution was warmed at 98 °C for 30 min. The resulting mixture was poured on crushed ice and extracted with dichloromethane. The extracts were washed with water, dried ($MgSO_4$) and concentrated to dryness. The residue was purified by column chromatography on silica gel. Elution with benzene–hexane (1 : 5) gave selenoxanthene (2) (4.3 g, 46.2%), which was recrystallized from methanol–dichloromethane to give colorless prisms, mp 145—146 °C (lit.,[11] mp 145 °C). Elution with benzene gave selenoxanthone (3) (4.9 g, 49.1%), which was recrystallized from ethanol to give pale yellow needles, mp 192—193 °C (lit.,[12] mp 191—192 °C).

9-Isopropylselenoxanthene (4)——*n*-Butyllithium (1.1 N in ether) (21 ml) was added to a suspension of **2** (4.9 g) in dry ether (80 ml) at room temperature, and the mixture was refluxed for 10 min. An ethereal solution (25 ml) of isopropyl iodide (4.1 g) was added to the cooled red solution, and then the mixture was refluxed for 6 h. Water was added to the cooled mixture and the organic layer was separated. The aqueous layer was extracted with ether. The organic layer and the extracts were combined, washed with water (20 ml × 2), dried ($MgSO_4$) and concentrated to dryness. The residue was purified by column chromatography on silica gel using chloroform–hexane (1 : 5) to afford 9-isopropylselenoxanthene (4) (4.3 g, 74.7%). Recrystallization from methanol gave colorless columns, mp 61.0—61.5 °C. NMR ($CDCl_3$) δ: 0.73 [6H, d, $J=6.6$ Hz, $CH(\underline{CH_3})_2$], 2.10—2.80 [1H, m, $\underline{C}H(CH_3)_2$], 3.52 (1H, d, $J=10.2$ Hz, C_9–H), 6.90—7.35 (6H, m, ArH), 7.35—7.70 (2H, m, $\underline{ArH}$). MS *m/e*: 288 (M^+, Se = 80), 245 (base peak). *Anal.* Calcd for $C_{16}H_{16}Se$: C, 66.90; H, 5.61. Found: C, 66.70; H, 5.59.

Selenoxanthene 10-Oxide (5a)——*m*-Chloroperbenzoic acid (85% pure) (1.82 g) was added to a solution of **2**

TABLE V. Physical Constants and Elemental Analyses of Selenoxantheniomethanides (**6a**—**i**)

Compd.	mp (°C) (dec.) (Recrystn. solvent[a])	EIMS *m/e* (Se = 80)	Formula	Analysis (%) Calcd (Found) C	H
6a	200—203 (A)	404 (M^+)	$C_{19}H_{16}O_5Se$	56.59 (56.33	4.00 3.95)
6b	177—179 (A)	432 (M^+)	$C_{21}H_{20}O_5Se$	58.48 (58.64	4.67 4.61)
trans-**6c**	187.5—188.5 (A)	388 (M^+)	$C_{20}H_{20}O_3Se$	62.02 (61.93	5.20 5.22)
trans-**6d**	242—245 (B)	387 ($M^+-CO_2CH_3$)[b]	$C_{22}H_{20}O_5Se$	59.33 (59.30	4.98 5.05)
trans-**6e**	154.5—156 (B)	474 (M^+) 401 ($M^+-CO_2C_2H_5$)	$C_{24}H_{26}O_5Se$	60.89 (60.98	5.54 5.58)
cis-**6f**	180.5—181.5 (C)	422 (M^+)	$C_{23}H_{18}O_3Se$	65.56 (65.36	4.31 4.30)
trans-**6f**	199—200 (C)	422 (M^+)	$C_{23}H_{18}O_3Se$	65.56 (65.53	4.31 4.36)
cis-**6g**	211—214 (B)	480 (M^+)	$C_{25}H_{20}O_5Se$	62.64 (62.28	4.21 4.07)
trans-**6g**	197—200 (B)	480 (M^+)	$C_{25}H_{20}O_5Se$	62.64 (62.54	4.21 4.12)
trans-**6h**	203—206 (A)	508 (M^+)	$C_{27}H_{24}O_5Se$	63.91 (63.88	4.77 4.64)
cis-**6i**	209—211 (B)	485 (M^+)	$C_{25}H_{15}D_5O_5Se$	485.0788[c] (485.0813)	
trans-**6i**	200—203 (B)	485 (M^+)	$C_{25}H_{15}D_5O_5Se$	485.0789[c] (485.0816)	

a) A, benzene–hexane; B, CH_2Cl_2–hexane; C, AcOEt–hexane.
b) A molecular ion peak was not observed. In the case of *trans*-**6e** the peak was very small.
c) High-resolution MS was used for elemental analysis because elemental analysis of the deuterated compounds could not be done on the elemental analyzer (Yanagimoto CHN corder MT-3).

(2.00 g) in dichloromethane (50 ml) at ice-bath temperature. After being stirred for 10 min, the reaction mixture was washed with saturated sodium hydrogen carbonate solution and water. The organic layer was dried ($MgSO_4$) and concentrated to dryness. The white crystals were washed with ether and then recrystallized from dichloromethane–hexane to give colorless plates (1.96 g, 92.0%), mp 139—140 °C (dec.). IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 805 (Se–O). NMR ($CDCl_3$) δ: 3.90 (1H, d, $J=16.2$ Hz, C_9–axial H), 4.32 (1H, d, $J=16.2$ Hz, C_9–equatorial H), 7.25—7.60 (6H, m, ArH), 7.75—8.10 (2H, m, $C_{4,5}$–H). MS *m/e*: 262 (M^+, Se=80). *Anal.* Calcd for $C_{13}H_{10}OSe$: C, 59.78; H, 3.86. Found: C, 59.61; H, 3.94.

9-Isopropylselenoxanthene 10-Oxide (5b)——In a manner similar to that described for the preparation of **5a**, **5b** (2.06 g, 97.6%) was obtained from **4** (2.00 g) and *m*-chloroperbenzoic acid (85% pure) (1.55 g). Recrystallization from methanol–ether gave colorless prisms, mp 166—167 °C. IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 825 (Se–O). NMR ($CDCl_3$) δ: 0.87 [6H, d, $J=6$ Hz, $CH(CH_3)_2$], 1.05—1.95 [1H, m, $C\underline{H}(CH_3)_2$], 3.75 (1H, d, $J=10.2$ Hz, C_9–H), 7.30—7.70 (6H, m, ArH), 7.90—8.20 (2H, $\underline{m, C_{4,5}}$–H). (C_6D_6) δ: 0.59 [6H, d, $J=6$ Hz, $CH(\underline{CH_3})_2$], 0.80—1.60 [1H, m, $C\underline{H}(CH_3)_2$], 3.29 (1H, d, $J=10.2$ Hz, C_9–H), 6.80—7.20 (6H, m, ArH), 7.98—8.30 (2H, $\underline{m, C_{4,5}}$–H). MS *m/e*: 304 (M^+, Se=80). *Anal.* Calcd for $C_{16}H_{16}OSe$: C, 63.37; H, 5.32. Found: C, 63.40; H, 5.22.

General Procedure for the Preparation of Selenoxantheniomethanides (6a—i)——An acetylenic compound was added to a solution of a selenoxanthene 10-oxide (**5a—d**). When the reaction was finished, the reaction mixture was concentrated to dryness. The residual solid was purified and recrystallized to give colorless prisms. Isomer ratios and yields are summarized in Table I and physicochemical data are listed in Table V.

Reaction of 9-Phenylselenoxanthene 10-Oxide (5c) with 10 eq of Methyl Propiolate——Methyl propiolate (4.99 g) was added to a solution of **5c**[3] (2.00 g) in dichloromethane (20 ml) at room temperature, and the mixture was refluxed for 72 h. The solvent was removed *in vacuo* and the residue was separated by column chromatography on silica gel. Elution with benzene–hexane (1 : 1) afforded 9-methoxy-9-phenylselenoxanthene (**10**) (165 mg, 7.9%). This product (**10**) was found to be identical with an authentic sample[13] by comparison of the IR and NMR spectra. Elution with benzene afforded methyl 9-phenylselenoxanthen-9-ylpropiolate (**9**) (527 mg, 22.0%) from the earlier fraction and 9-phenylselenoxanthenol (**7**) (656 mg, 26.3%) from the later fraction. Recrystallization of **9** from benzene–hexane gave colorless prisms, mp 171—173 °C. IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 2235 ($C\equiv C$), 1715 (C=O). NMR ($CDCl_3$) δ: 3.80 (3H, s, CO_2CH_3), 6.60—6.95 (2H, m, ArH), 6.95—7.70 (9H, m, ArH), 8.15—8.37 (2H, m, ArH). MS *m/e*: 404 (M^+, Se=80). *Anal.* Calcd for $C_{23}H_{16}O_2Se$: C, 68.49; H, 4.00. Found: C, 68.53; H, 3.90. Elution with benzene–ethyl acetate (1 : 1) afforded *cis*-**6f** (65 mg, 2.6%) from the earlier fraction and *trans*-**6f** (608 mg, 24.3%) from the later fraction.

TABLE VI. Physical Constants and Elemental Analyses of 3-(Selenoxanthen-10-io)-2,4-dioxooxolan-3-ides (**16a—c**) and Selenoxanthen-10-io(hydroxyacetyl ethoxycarbonyl)methanides (**17a—f**)

Compd.	mp (°C) (dec.) (Recrystn. solvent[a])	Formula	Analysis (%) Calcd (Found)	
			C	H
16a	196—199 (AcOEt)	$C_{17}H_{12}O_3Se$	59.49 (59.37	3.52 3.42)
trans-**16b**	243—244 (B)	$C_{20}H_{18}O_3Se$	62.34 (62.11	4.71 4.68)
trans-**16c**	229—231 (Acetone)	$C_{23}H_{16}O_3Se$	65.88 (65.94	3.85 3.78)
17a	177—180 (AcOEt)	$C_{18}H_{16}O_4Se$	57.61 (57.65	4.30 4.31)
17b	177—178 (A)	$C_{19}H_{18}O_4Se$	58.62 (58.77	4.66 4.67)
trans-**17c**	213.5—214.5 (A)	$C_{21}H_{22}O_4Se$	60.43 (60.30	5.31 5.27)
trans-**17d**	191.5—193 (A)	$C_{22}H_{24}O_4Se$	61.25 (61.09	5.61 5.54)
trans-**17e**	200.5—201.5 (A)	$C_{24}H_{20}O_4Se$	63.86 (63.67	4.47 4.46)
trans-**17f**	182.5—183.5 (AcOEt)	$C_{25}H_{22}O_4Se$	64.52 (64.80	4.76 4.63)

a) A, AcOEt–hexane; B, CH_2Cl_2–hexane.

General Procedure for the Reduction of Selenoxantheniomethanides with Sodium Borohydride——Sodium borohydride was added to a solution of a selenoxantheniomethanide at room temperature. When the reaction was finished, the reaction mixture was poured into water and extracted with dichloromethane. The extracts were washed with water, dried ($MgSO_4$) and concentrated to dryness. The residue was purified and recrystallized to give colorless prisms. Products and yields are summarized in Table III and physical data are listed in Table VI.

Cyclization of 17b to 16a——a) Potassium carbonate (124 mg) was added to a solution of **17b** (70 mg) in a mixture of ethanol (10 ml), dichloromethane (5 ml) and water (5 ml). After being stirred for 6 h at room temperature, the reaction mixture was poured into water and extracted with dichloromethane. The extracts were washed with water, dried (K_2CO_3) and concentrated to dryness. The crude crystals were recrystallized from dichloromethane–ether to afford a colorless powder (**16a**) (52 mg, 84.3%).

b) Sodium borohydride (34 mg) was added to a solution of **17b** (70 mg) in ethanol (10 ml) at room temperature. After being stirred for 42 h the reaction mixture was worked up as in a) to afford **16a** (46 mg, 74.6%).

References and Notes

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