Reactions of 10-Alkyl- and 10-Aryl-9-phenylthioxanthenium Salts with Various Bases—— 1,4-Sigmatropic Rearrangement of 10-Alkyl- and 10-Aryl-9-phenyl-9-thiaanthracenes

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Abstract : A 1,4-sigmatropic rearrangement of 10-alkyl and 10-aryl-9-phenyl-10-thiaanthracenes is described. 10-(4-Methoxyphenyl)-9-phenyl-10-thiaanthracene generated by proton abstraction of 10-(4-methoxyphenyl)-9-phenylthioxanthenium perchlorate (**1a**) with bases such as sodium dimsylate, sodium methoxide, sodium hydride, and Grignard reagent underwent 1,4-rearrangement to afford 9-(4-methoxyphenyl)-9-phenylthioxanthene (**2a**) in high yield. The deprotonation of **1a** with organolithiums such as phenyllithium or methyllithium afforded 9,9-diphenylthioxanthene (**3**) or 9-methyl-9-phenylthioxanthene (**2d**) *via* ligand-exchanged thiaanthracene intermediates generated *in situ,* along with **2a**. Other 10-alkyl or 10-aryl-9-phenylthiaanthracenes generated from the corresponding thioxanthenium salts (**1b-g**) by treatment with base also decomposed thermally to give 1,4-rearranged products **2b-g** in good yield. These 1,4-rearrangements were found to be intramolecular 1,4-sigmatropic rearrangements by cross over experiments.

Keyphrases : thiaanthracene, thioxanthenium salt, 1,4-sigmatropic rearrangement, cross over reaction, 1,4-cyclic ylide, thioxanthene, organolithium, ligand exchange, steric hindrance

Extensive studies have been made on the reactions of sulfonium salts with bases[1]. On sulfonium salts bearing no hydrogen atom at the α-position, as in the case of triaryl sulfonium salts and related compounds, some bases having nucleophilicity attack positively charged sulfur atoms to generate σ-sulfurane intermediates, which may then undergo a wide variety of subsequent reactions or cause ligand exchange reaction, or attack the α-carbon atom to release sulfides. On sulfonium salts bearing the α,β-unsaturated bond, bases alsonucleophilically attack the β-position (Michael addition reaction) to afford new sulfonium salts or sulfonium ylides. Sulfonium salts bearing a hydrogen atom at α-position undergo deprotonation of hydrogen by treatment with strong bases to give sulfonium ylides[2]. Sulfonium ylides in which carbanion electrons are delocalized to electron-withdrawing groups such as carbonyl, sulfonyl, cyano, or nitro substituents, or cyclic conjugated polyene that enhances aromaticity are stabilized and can be isolated. Otherwise, sulfonium ylides are unstable and undergo various types of degradation reactions.

We now investigated reactions of cyclic sulfonium salts bearing active hydrogen atom at the γ-position

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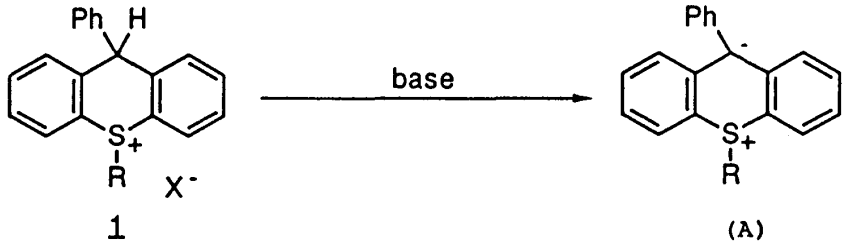
to sulfur atom, 10-alkyl- or 10-aryl-9-phenylthioxanthenium salts (**1**), with several bases, for the determination of the stability and structures of the 1,4-cyclic ylides, 10-alkyl and 10-aryl-9-phenyl-10-thiaanthracenes (A) generated by the above reactions.



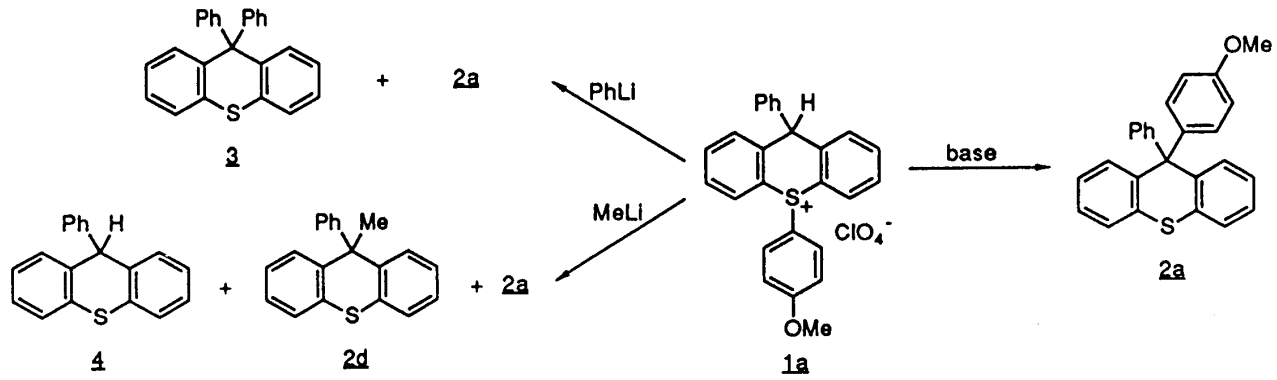
Scheme 1

Thiaanthracenes (A) easily underwent 1,4-rearrangement to afford the corresponding 9,9-disubstituted thioxanthenes in good yield, and organolithium reagents as bases attacked sulfur atoms to cause ligand exchange reactions, with subsequent 1,4-rearrangement[3].

Results and Discussion

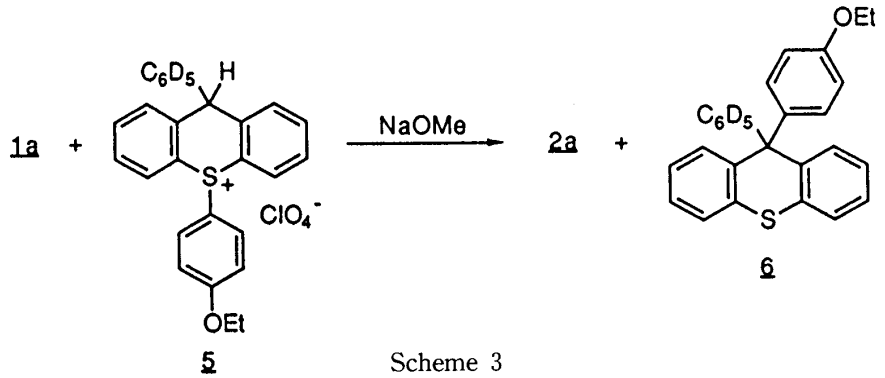
Treatment of 10-(4-methoxyphenyl)-9-phenylthioxanthenium perchlorate (**1a**) with sodium dimsylate in DMSO under nitrogen atmosphere at room temperature caused the 1,4-migration of the 10-methoxyphenyl group to afford 9-(4-methoxyphenyl)-9-phenylthioxanthene (**2a**), mp 217-218℃ in 95% yield. Treatment of **1a** with other bases such as sodium hydride in tetrahydrofuran (THF), sodium methoxide in boiling methanol, and phenylmagnesium bromide in boiling benzene gave the 1,4-rearranged product **2a** in 91%, 87% and 74 % yield, respectively. On the contrary, reaction of **1a** with organolithium reagents as bases gave new products in addition to the 1,4-rearranged product. Treatment of **1a** with excess phenyllithium in ether at room temperature gave a 39% yield of 9,9-diphenylthioxanthene (**3**), mp 217℃ along with 60% yield of **2a**. The structure of **3** was determined using an authentic specimen, as confirmed by comparison of IR and ^{1}H-NMR spectra. Similar results were obtained from the reaction with excess methyllithium as a base to afford 9-methyl-9-phenylthioxanthene (**2d**) in 16% yield along with 45% yield of **2a** and 23% yield of 9-phenylthioxanthene (**4**) which could not be obtained by reaction with phenyllithium. The formation of **3** or **2d** strongly suggests that organolithium reagents nucleophilically attack trivalent sulfur atoms with subsequent ligand exchange reaction[4].

In order to investigate the scope and generality of the above 1,4-rearrangement reactions, we studied the reactions of several other 10-aryl- (**1b, c**) and 10-alkylthioxanthenium salts (**1d-g**) with various bases. The results are summarized in Table. In the case of 10-aryl derivatives (**1b, c**), 1,4-rearranged products were obtained in very high yield (entries 1, 2). However, when phenyllithium was used as a base, ligand-exchanged 1,4-rearrangement product **3** was produced as in the case of **1a** (entry 3). On the other hand, 10-alkyl derivatives **1d-g** underwent partially dealkylation to give 9-phenylthioxanthene (**4**) in addition to 1,4-rearranged products in all cases. Treatment with weak base such as triethylamine afforded only dealkylated product in high yield (entry 6).



Scheme 2

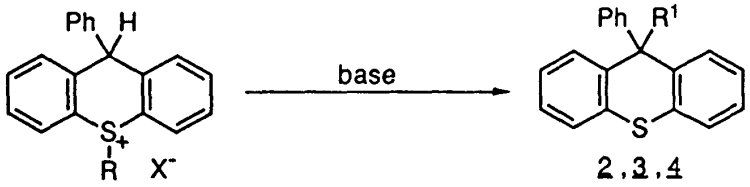
We next carried out the cross over reaction to determine whether the above 1,4-rearrangements of thioxanthenium salts caused by base proceeds intramolecularly or intermolecularly. Treatment of a mixture of **1a** and 10-(4-ethoxyphenyl)-9-(pentadeuteriophenyl) thioxanthenium perchlorate (**5**) with sodium methoxide in refluxing methanol afforded **2a** and 9-(4-ethoxyphenyl)-9-(pentadeuteriophenyl) thioxanthene (**6**), mp 174 ℃ in a ratio of 1 : 1, but no crossed products. The mass spectrum of the above reaction mixture showed no detectable molecular ion peaks due to the crossed products. The 1,4-rearrangement would thus appear to proceed intramolecularly. Moreover, when 9-phenyl-10-propylthioxanthenium salt (**1f**) was allowed to react with a base, no product bearing an isopropyl group at 9-position, possibly produced by the isomerization of propyl group during rearrangement, assuming rearrangement to proceed intermolecularly *via* propyl carbocation intermediate, was obtained as shown in Table. From reactions of thioxanthenium salts **1a-c** with sodium methoxide in methanol, 9-methoxy-9-phenylthioxanthene was not obtained, which may be intermolecularly formed by Pummerer-type rearrangement *via* thioxanthylium ion intermediate.



Scheme 3

From the above results and consideration that the 1,4-rearrangements of the present compounds may be formed by symmetrically allowed 1,4-sigmatropic rearrangement of a six-electrons system according to the Woodward-Hoffmann rule, we propose the following mechanism for the 1,4-rearrangement of 10-substituted 9-phenylthioxanthenium salts to 9-substituted 9-phenylthioxanthene by treatment with bases including organolithium reagents (Scheme 4).

Table. Reactions of 10-Alkyl- and 10-Aryl-9-phenylthioxanthenium Salts with Various Bases



1 2, 3, 4

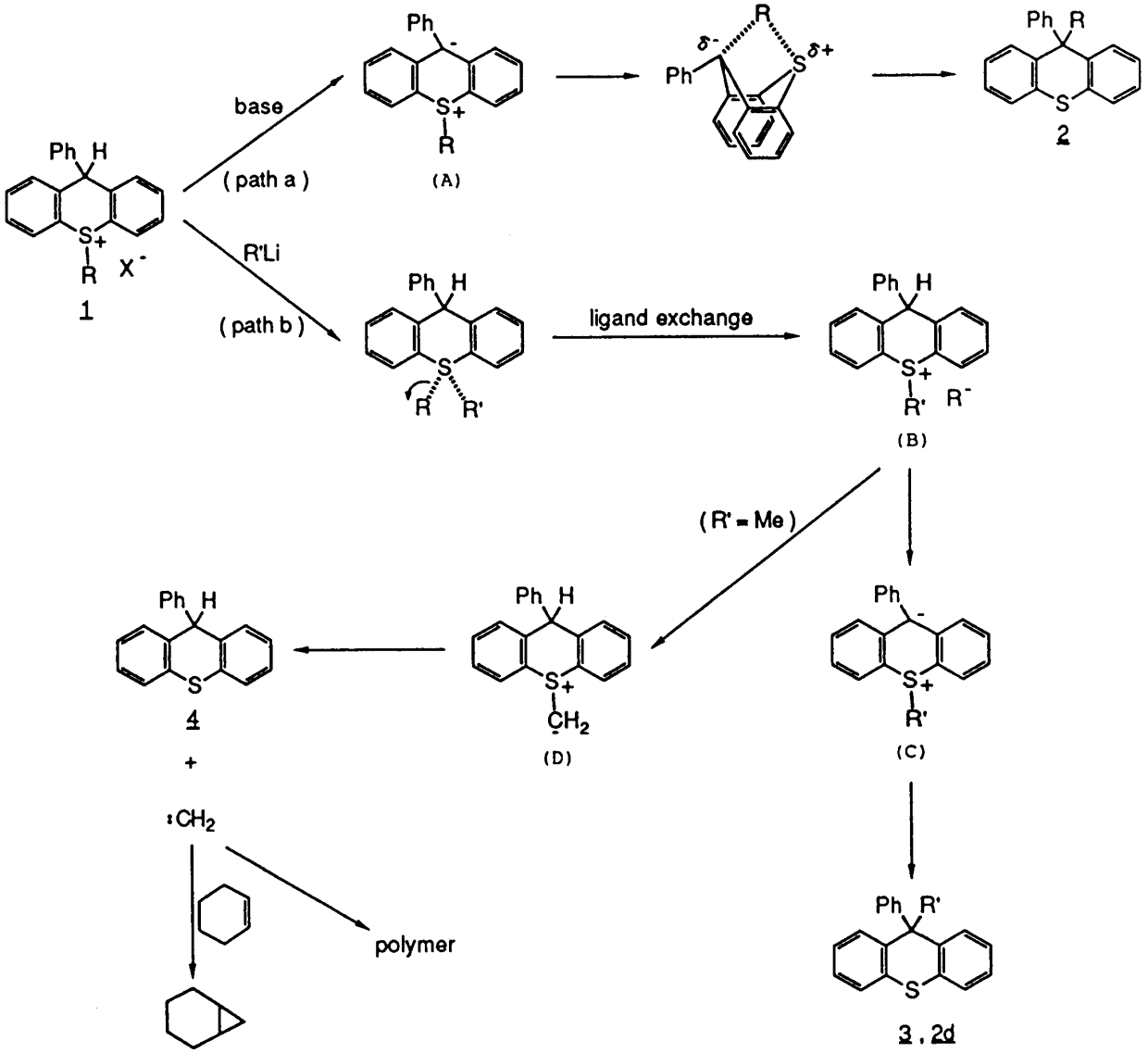
entry No.	thioxanthenium salt (1) compd. No.	R	X	base	solvent	products R^1 (No.)[a]	yield (%)
1	1b	4-$EtOC_6H_4$	ClO_4	NaOMe	MeOH	4-$EtOC_6H_4$ (2b)	98
2	1c	2,4-$(MeO)_2C_6H_3$	ClO_4	NaOMe	MeOH	2,4-$(MeO)_2C_6H_3$ (2c)	94
3	1c			PhLi	ether	2,4-$(MeO)_2C_6H_3$ (2c)	9
						Ph (3)	86
4	1d	Me	BF_4	$NaCH_2SOMe$	DMSO	Me (2d)	70
						H (4)	21
5	1d			t-BuOK	DMSO	Me (2d)	80
						H (4)	13
6	1d			Et_3N	EtOH	H (4)	91
7	1d			PhLi	ether	Me (2d)	10
						H (4)	89
8	1d			MeLi	ether	Me (2d)	29
						H (4)	68
9	1e	Et	BF_4	t-BuOK	DMSO	Et (2e)	90
						H (4)	5
10	1f	Pr	ClO_4	t-BuOK	DMSO	Pr (2f)	52
						H (4)	10
11	1g	s-Bu	BF_4	$NaCH_2SOMe$	DMSO	s-Bu (2g)	10
						H (4)	42

a : Compd. No.

Thioxanthenium salts (**1**) are deprotonated at the 9-position with a base to give zwitter ionic intermediates (thiaanthracenes (A)), which successively rearrange intramolecularly to give 1,4-rearranged products **2** (path a). Organolithiums (R'Li) as bases attack the positively charged sulfur atom of **1** as nucleophiles resulting in ligand exchange and new thioxanthenium ion intermediates (B) are formed (path b). The thioxanthenium ions (B) are deprotonated at the 9-position with the released ligand (R^-) or excess organolithium (R'^-) to afford ligand-exchanged rearrangement products **3** and **2d**. When R' is methyl group in the intermediate (B), bases may possibly deprotonate from the methyl group to afford methylide intermediate (D), which decomposes to methylene and 9-phenylthioxanthene (**4**). The deprotonation of 10-methyl-9-phenylthioxanthenium salt (**1d**) with various bases afforded **4** along with a 1,4-rearranged product (**2d**). Methylene was polymerized the most, but it was partly trapped with cyclohexene to afford norcarane detectable by GC.

A major product from the reaction of 10-(2,4-dimethoxyphenyl)-9-phenylthioxanthenium perchlorate (**1c**) with phenyllithium was a ligand-exchanged rearrangement product, 9,9-diphenylthioxanthene (**3**) (86%) (entry 3 of Table). This might be explained in terms of the steric hindrance of the ortho methoxy group of 10-

substituent which would play a role in preventing the 10-substituent from migrating to the 9-position, consequently causing a ligand exchange reaction leading to the formation of product **3** *via* the 9,10-diphenylthiaanthracene intermediate.



Scheme 4

Experimental

Melting points were determined on a Yanagimoto micromelting point apparatus and are uncorrected. Infrared (IR) absorption spectra were determined on a JASCO IR A-1 infrared spectrometer. Proton nuclear magnetic resonance (^{1}H-NMR) spectra were taken on a Hitachi R-20B spectrometer, and chemical shifts were given in ppm with tetramethylsilane as the internal standard (s, singlet ; d, doublet ; t, triplet ; m, multiplet). Mass spectra (MS) were recorded on a JEOL JMSD-300 spectrometer with a JMA 2000 on-line system at 70 eV. Analytical and preparative thin-layer chromatography were performed using E.M. Merk silica gel 60PF-254.

Materials. The following compounds were previously synthesized by our and other groups. 9-Phenylthioxanthene (**4**)[5], 9-(pentadeuteriophenyl)thioxanthene[6], 9-phenylthioxanthene 10-oxide[6], 9-(pentadeuteriophenyl)thioxanthene 10-oxide[6], 10-methyl-9-phenylthioxanthenium tetrafluoroborate (**1d**)[7a,c], 10-ethyl-9-phenylthioxanthenium tetrafluoroborate (**1e**)[7a,c], and 9-phenyl-10-propylthioxanthenium perchlorate (**1f**)[7a,c].

10-(4-Methoxyphenyl)-9-phenylthioxanthenium Perchlorate (1a)——Concentrated sulfuric acid (1.5 ml) was added to an ice-cooled solution of 9-phenylthioxanthene 10-oxide[6] (1 g, 3.45 mmol) in anisole (8 ml) with stirring and the mixture was stirred for 3.5 days at room temperature. The reaction mixture was poured into ice-water and extracted with ether to remove ether-soluble materials. 70% Perchloric acid (3 ml) was added to the separated water layer to precipitate the white crystals which were subsequently extracted with dichloromethane. The extract was washed with water, dried ($MgSO_4$), and concentrated under reduced pressure to give 1.32 g (74%) of crystals (**1a**) as a mixture of cis and trans stereoisomers. These were partially separated by careful fractional recrystallization from butanol. trans Isomer[7] : mp 210-211℃, colorless plates, IR (KBr) cm^{-1} : 1080 (ClO_4^-). ^{1}H-NMR (CF_3CO_2H) δ : 4.07 (3H, s, OMe), 5.80 (1H, s, 9-H), 6.90-7.20 (2H, m, 2,6-H of 9-Ph), 7.25-7.70 (3H, m, 3,4,5-H of 9-Ph), 7.52 (4H, A_2B_2 q, J= 9 Hz, 2,3,5,6-H of 10-Ar), 7.75-7.90 (8H, m, other ArH). ^{1}H-NMR (DMSO-d_6) δ : 3.97 (3H, s, OMe), 6.27 (1H, s, 9-H), 7.00-8.00 (17H, m, ArH). *Anal.* Calcd for $C_{26}H_{21}ClO_5S$: C, 64.92 ; H, 4.40. Found : C, 64.68 ; H, 4.39. cis-Isomer[7] : mp 154℃ (This isomer crystallized after melting at 154℃ and then again melted at the melting point (211-212℃) of the trans isomer. The cis isomer thus easily isomerizes to the trans isomer on heating beyond the melting point.), colorless prisms, IR (KBr) cm^{-1} : 1100 (ClO_4^-). ^{1}H-NMR (CF_3CO_2H) δ : 3.87 (3H, s, OMe), 5.82 (1H, s, 9-H), 6.55-6.75 (2H, m, 2,6-H of 9-Ph), 6.80-7.12 (3H, m, 3,4,5-H of 9-Ph), 6.85 (4H, A_2B_2 q, J= 9 Hz, 2,3,5,6-H of 10-Ar), 7.75-8.28 (8H, m, other ArH). ^{1}H-NMR (DMSO-d_6) δ : 3.73 (3H, s, OMe), 6.12 (1H, S, 9-H). *Anal.* Calcd for $C_{26}H_{21}ClO_5S$: C, 64.92 ; H, 4.40. Found : C, 64.79 ; H, 4.64. The ratio of cis and trans isomers was 1 : 3 by ^{1}H-NMR measurement of a crude mixture of **1a**.

In a similar manner as above, the following 10-aryl-9-phenylthioxanthenium perchlorates were prepared.

10-(4-Ethoxyphenyl)-9-phenylthioxanthenium Perchlorate (1b) (1.28 g, 75.3%), from 9-phenylthioxanthene 10-oxide (1 g, 3.45 mmol), phenetole (9.3 ml), conc. sulfuric acid (1.5 ml). Recrystallization from methanol afforded only one isomer (trans isomer)[7a,c] in pure form, mp 226.5-227.5℃, colorless plates, IR (KBr) cm^{-1} : 1090 (ClO_4^-) ; ^{1}H-NMR (DMSO-d_6) δ : 1.39 (3H, t, J= 7 Hz, CH_2CH_3), 4.23 (2H, q, J= 7 Hz, CH_2CH_3), 6.26 (1H, s, 9-H), 7.04-8.00 (17H, m, ArH). *Anal.* Calcd for $C_{27}H_{23}ClO_5S$: C, 65.51 ; H, 4.68. Found : C, 65.43 ; H, 4.74. In the ^{1}H-NMR spectrum (DMSO-d_6) of the crude product, signals corresponding to the other isomer (cis isomer) were observed : 1.28 (3H, t, J= 7 Hz, CH_2CH_3), 4.01 (2H, q, J= 7 Hz, CH_2CH_3), 6.11 (1H, s, 9-H).

10-(2,4-Dimethoxyphenyl)-9-phenylthioxanthenium Perchlorate (1c) (1.59 g, 82.9%), from 9-phenylthioxanthene 10-oxide (1 g, 3.45 mmol), *m*-dimethoxybenzene (9.7 ml), conc. sulfuric acid (1.5 ml).

Recrystallization from methanol gave only one isomer (trans isomer)[7] in pure form, mp 236℃, colorless plates, IR (KBr) cm^{-1} : 1100 (ClO_4^-). ^1H-NMR (DMSO-d_6) δ : 3.58 (3H, s, OMe), 3.99 (3H, s, OMe), 6.20 (1H, s, 9-H), 6.90-8.00 (16H, m, ArH). *Anal.* Calcd for $C_{27}H_{23}ClO_6S$: C, 63.46 ; H, 4.54. Found : C, 63.23 ; H, 4.51. ^1H-NMR (DMSO-d_6) of the crude product showed the presence of the other isomer (cis isomer) : 3.77 (3H, s, OMe), 4.05 (3H, s, OMe), 5.95 (1H, s, 9-H).

10-*s*-Butyl-9-phenylthioxanthenium Tetrafluoroborate (1g)——Silver tetrafluoroborate (700 mg, 3.6 mmol) was added portionwise to a stirred solution of 9-phenylthioxanthene (**4**)[5] (1 g, 3.6 mmol) and *s*-butyl bromide (3 g, 22 mmol) in dichloromethane (10 ml) followed by stirring for 6 h at room temperature. The precipitate was filtered off and the filtrate was diluted with ether to give 300 mg (19.7%) of **1g**. Recrystallization from dichloromethane-ether afforded colorless plates, mp 117.5℃, IR (KBr) cm^{-1} : 1080 (BF_4^-). ^1H-NMR ($CDCl_3$) δ : 0.55 (3H, t, J=6 Hz, CH_2CH_3), 1.15 (3H, d, J=7 Hz, $CHCH_3$), 1.20 (2H, m, $-CH_2-$), 2.76 (1H, m, CH-), 5.78 (1H, s, 9-H), 6.70-8.20 (12H, m, ArH). *Anal.* Calcd for $C_{23}H_{23}BF_4S$: C, 66.04 ; H, 5.54. Found : C, 66.05 ; H, 5.55.

Reactions of 10-(4-Methoxyphenyl)-9-phenylthioxanthenium Perchlorate (1a) with Bases——

a) **with Sodium Dimsylate in DMSO** : Sodium hydride (113 mg, 4.68 mmol) was added to dry DMSO (4 ml), and the mixture was stirred for 2 h at 70-75℃ under nitrogen atmosphere. After cooling, a solution of **1a** (1.5 g, 3.12 mmol) in dry DMSO (6 ml) was added and the mixture was stirred for 5 h at room temperature. The reaction mixture was poured into ice-water and extracted with chloroform. The extract was washed with water, dried ($MgSO_4$) and evaporated. The residual solids were recrystallized from benzene-pet. ether to give 1.1 g of 9-(4-methoxyphenyl)-9-phenylthioxanthene (**2a**) as colorless plates, mp 218℃, ^1H-NMR ($CDCl_3$) δ : 3.78 (3H, s, OMe), 6.58-7.52 (17H, m, ArH). *Anal.* Calcd for $C_{26}H_{20}OS$: C, 82.07 ; H, 5.30. Found : C, 81.93 ; H, 5.43.

b) **with Sodium Hydride in THF** : Sodium hydride (50% dispersion in mineral oil, 248 mg, 5.16 mmol) was added in one portion to a stirred suspension of **1a** (413 mg, 0.86 mmol) in dry THF (30 ml) under nitrogen atmosphere, and the mixture was stirred for 5 h at room temperature. The reaction mixture was poured into ice-water and extracted with dichloromethane. The extract was washed with water, dried (K_2CO_3) and evaporated to dryness to give 300 mg of **2a**.

c) **with Sodium Methoxide in Methanol** : Powdered **1a** (585 mg, 1.22 mmol) was added to a stirred solution of sodium (170 mg, 7.3 mmol) dissolved in dry methanol (50 ml), and the mixture was stirred for 2 h at room temperature and refluxed for 5 h. The reaction mixture was poured into water and extracted with chloroform. The extract was washed with water, dried ($MgSO_4$) and evaporated to afford 404 mg of **2a**.

d) **with Phenylmagnesium Bromide in Benzene** : An ethereal solution of phenylmagnesium bromide was prepared from Mg (0.3 g) and bromobenzene (1.8 g) in dry ether as usual. Dry benzene (40 ml) was added to the above Grignard solution and ether was evaporated off. Powdered **1a** (622 mg, 1.3 mmol) was added to the benzene solution of Grignard reagent, and the mixture was refluxed for 26 h under an N_2 atmosphere.

The reaction mixture was hydrolyzed by adding a sat. ammonium chloride solution and extracted with dichloromethane. The extract was washed with water, dried ($MgSO_4$), and evaporated to dryness. The residue was subjected to preparative TLC on silica gel using hexane-benzene (5 : 1) to afford 363 mg of **2a** and 27 mg of 9-phenylthioxanthene (**4**).

e) **with Phenyllithium in Ether** : Powdered **1a** (500 mg, 1.04 mmol) was added under an N_2 atmosphere to an ethereal solution of 1.1 *N* phenyllithium (5.7 ml), and the mixture was stirred for 6 h at room temperature. The reaction mixture was hydrolyzed with a sat. ammonium chloride solution and extracted with dichloromethane. The extract was washed with water, dried ($MgSO_4$) and concentrated to dryness. The residual oil was subjected to preparative TLC on silica gel using hexane-benzene (5 : 1) as solvent to afford 230 mg of **2a** and 112 mg of 9,9-diphenylthioxanthene (**3**) as colorless plates, mp 217-218℃. ^{1}H-NMR ($CDCl_3$) δ : 6.70-7.50 (m, ArH). *Anal.* Calcd for $C_{25}H_{18}S$: C, 85.67 ; H, 5.18. Found : C, 85.54 ; H, 5.36.

f) **with Methyllithium in Ether** : Powdered **1a** (568 mg, 1.18 mmol) was added under nitrogen atmosphere to an ethereal solution of methyllithium, prepared from methyl iodide (2.84 g), Li (0.32 g) and dry ether (20 ml) as usual, and the mixture was stirred for 6 h. Work-up as above left an oily product which was subjected to preparative TLC on silica gel using hexane-benzene (5 : 1) to give 153 mg of **2a**, 53.2 mg of **4** and 79.8 mg of 9-methyl-9-phenylthioxanthene (**2d**) as colorless needles after recrystallization from methanol, mp 138 ℃, ^{1}H-NMR ($CDCl_3$) δ : 2.04 (3H, s, Me), 6.70-7.50 (13H, m, ArH). *Anal.* Calcd for $C_{20}H_{16}S$: C, 83.28 ; H, 5.59. Found : C, 83.02 ; H, 5.80.

Reaction of 10-(4-Ethoxyphenyl)-9-phenylthioxanthenium Perchlorate (1b) with Sodium Methoxide—— Powdered **1b** (1 g, 2.02 mmol) was added to a stirred solution of sodium (280 mg, 12.2 mmol) in dry methanol (60 ml), and the mixture was stirred for 7 h at room temperature. Work-up as for **1a** afforded a crude crystal, which was recrystallized from ethanol to give 780 mg of 9-(4-ethoxyphenyl)-9-phenylthioxanthene (**2b**) as colorless columns, mp 180-180.5℃, ^{1}H-NMR ($CDCl_3$) δ : 1.40 (3H, t, J= 7 Hz, CH_2CH_3), 4.00 (2H, q, J= 7 Hz, CH_2CH_3), 6.70-7.60 (17H, m, ArH). *Anal.* Calcd for $C_{27}H_{22}OS$: C, 82.20 ; H, 5.62. Found : C, 82.03 ; H, 5.70.

Reactions of 10-(2,4-Dimethoxyphenyl)-9-phenylthioxanthenium Perchlorate (1c) with Bases——

a) **with Sodium Methoxide in Methanol** : Powdered **1c** (646 mg, 1.26 mmol) was added portionwise to a solution of sodium (180 mg, 7.8 mmol) in dry methanol (60 ml), and the mixture was stirred for 7 h at room temperature. The reaction mixture was poured into water and extracted with dichloromethane. The extract was washed with water, dried (K_2CO_3) and evaporated to dryness. The residue was purified by preparative TLC on silica gel using benzene-hexane (1 : 5) as solvent to afford 487 mg of 9-(2,4-dimethoxyphenyl)-9-phenylthioxanthene (**2c**) which was recrystallized from methanol-benzene to form colorless plates, mp 171℃, ^{1}H-NMR ($CDCl_3$) δ : 3.30 (3H, s, OMe), 3.84 (3H, s, OMe), 6.35-7.50 (16H, m, ArH). MS *m/z* : 410 (M^+), 379 (M^+-OMe), 333 (M^+-Ph), 273 (M^+-2MeO-C_6H_4). *Anal.* Calcd for $C_{27}H_{22}O_2S$: C, 78.99 ; H, 5.41. Found : C, 79.02 ; H, 5.60.

b) **with Phenyllithium in Ether** : In a similar manner as with **1a**, **1c** (500 mg, 0.98 mmol) was allowed

to react with 6 eq of phenyllithium in ether (30 ml) for 5 h at room temperature and worked up to give 297 mg of **3** and 34 mg of **2c** after separation with preparative TLC on silica gel using benzene-hexane (1 : 5) as solvent.

Reactions of 10-Alkyl-9-phenylthioxanthenium Salts (1d-g) with Bases——

a) **with Sodium Dimsylate in DMSO** : A solution of 10-methyl-9-phenylthioxanthenium tetrafluoroborate (**1d**)[7a,c] (377 mg, 1.00 mmol) in DMSO (5 ml) was added to a DMSO solution of sodium dimsylate prepared from sodium hydride (66 mg, 2.75 mmol) and DMSO as described above and the mixture was stirred for 3 h. Work-up as with **1a** afforded 220 mg of **2d** and 58 mg of **4**.

In a similar manner as above, treatment of 10-*s*-butyl-9-phenylthioxanthenium tetrafluoroborate (**1g**) (443 mg, 1.1 mmol) with sodium dimsylate in DMSO provided 122 mg of **4** and 35 mg of 9-*s*-butyl-9-phenylthioxanthene (**2g**). The latter was recrystallized from ethanol-dichlormethane to form colorless plates, mp 115℃, ^{1}H-NMR (CCl_4) δ : 0.81 (3H, t, J= 6 Hz, CH_2CH_3), 0.87 (3H, d, J= 6.5 Hz, $CHCH_3$), 1.50-1.95 (2H, m, CH_2), 2.10-2.70 (1H, m, -CH-), 6.59-7.35 (13H, m, ArH). MS *m/z* : 330 (M^+). *Anal.* Calcd for $C_{23}H_{22}S$: C, 83.58 ; H, 6.71. Found : C, 83.37 ; H, 6.74.

b) **with Phenyllithium in Ether** : In the similar manner as with **1a**, reaction of **1d** (1 g, 2.66 mmol) with 1.5 *N* Phenyllithium in ether (10 ml) for 6 h at room temperature gave 657 mg of **4** and 76 mg of **2d**.

c) **with Methyllithium in Ether** : In a similar manner as with **1a**, treatment of **1d** (1 g, 2.55 mmol) with an ethereal solution of methyllithium, prepared from Li (230 mg, 33.1 mmol) and methyl iodide (2.3 g, 16.2 mmol) as usual, at room temperature for 6 h gave 490 mg of **4** and 220 mg of **2d**.

d) **with Potassium *t*-Butoxide in DMSO** : Powdered **1d** (500 mg, 1.33 mmol) was added to a solution of potassium *t*-butoxide (1 : 1 complex with *t*-butanol, 250 mg, 1.33 mmol) in DMSO (7 ml), and the mixture was stirred for 6 h at room temperature under an N_2 atmosphere. The reaction mixture was poured into ice-water and worked up to give 50 mg of **4** and 300 mg of **1d**.

In a similar manner as above, treatment of 10-ethyl-9-phenylthioxanthenium tetrafluoroborate (**1e**)[7a,c] (500 mg, 1.28 mmol) with potassium *t*-butoxide (400 mg, 2.13 mmol) in DMSO (15 ml) for 6 h at room temperature afforded 17 mg of **4** and 349 mg of 9-ethyl-9-phenylthioxanthene (**2e**) as an oil (210℃/1 mmHg), ^{1}H-NMR ($CDCl_3$) δ : 0.78 (3H, t, J= 7 Hz, CH_2CH_3), 2.35 (2H, q, J= 7.5 Hz, CH_2CH_3), 6.70-7.50 (13H, m, ArH). *Anal.* Calcd for $C_{21}H_{18}S$: C, 83.40 ; H, 6.00. Found : C, 83.44 ; H, 6.21.

In a similar manner as above, reaction of 9-phenyl-10-propylthioxanthenium perchlorate (**1f**)[7a,c] (700 mg, 1.68 mmol) with potassium *t*-butoxide (320 mg, 1.70 mmol) in DMSO (16 ml) for 8 h at room temperature gave 46 mg of **4** and 276 mg of 9-phenyl-9-propylthioxanthene (**2f**), mp 101℃, ^{1}H-NMR ($CDCl_3$) δ : 0.86 (3H, t, J= 6 Hz, CH_2CH_2Me), 1.20 (2H, m, CH_2CH_2Me), 2.30 (2H, t, J= 6.5 Hz, CH_2CH_2Me), 6.70-7.50 (13H, m, ArH). *Anal.* Calcd for $C_{22}H_{20}S$: C, 83.48 ; H, 6.37. Found : C, 83.49 ; H, 6.54.

e) **with Triethylamine in Ethanol** : A mixture of **1d** (500 mg, 1.33 mmol) and triethylamine (270 mg, 2.67 mmol) in ethanol (20 ml) was stirred for 6 h at room temperature. The reaction mixture was concentrated to dryness and extracted with ether. The extract was evaporated off to give 330 mg of **4**.

10-(4-Ethoxyphenyl)-9-(pentadeuteriophenyl)thioxanthenium Perchlorate (5)——Phenetole (1.89 g, 15 mmol) was added to an ice-cooled mixture of 70% perchloric acid (5.4 ml) and $POCl_3$ (4.3 ml). 9-(Pentadeuteriophenyl)thioxanthene 10-oxide[6] (3 g, 10 mmol) was slowly added to the above solution, and the mixture was stirred for two days. The reaction mixture was poured into ice-water and ether was added to precipitate crystals which were collected by filtration. Recrystallization from butanol gave 810 mg of **5** as colorless needles, mp 225-226℃, IR (KBr) cm^{-1} : 1070 (ClO_4^-). ^1H-NMR (CF_3CO_2H) δ : 1.54 (3H, t, J= 7 Hz, CH_2CH_3), 4.29 (2H, q, J= 7 Hz, CH_2CH_3), 5.78 (1H, s, 9-H), 7.22-7.94 (12H, m, ArH). *Anal.* Calcd for $C_{27}H_{18}ClDO_5S$: C, 64.85 ; H, 5.64. Found : C, 64.67 ; H, 5.68.

Reaction of a Mixture of 1a and 5 with Sodium Methoxide (Cross Over Experiment)——A powdered mixture of **1a** (1 g, 2.1 mmol) and **5** (1.04 g, 2.1 mmol) was added in one portion to a stirred solution of Na (574 mg, 25 mmol) dissolved in dry methanol (150 ml), and the mixture was stirred for 5 h at room temperature, then refluxed for 3.5 h. The reaction mixture was poured into ice-water and extracted with dichloromethane. The extract was washed with water, dried (K_2CO_3), and evaporated to dryness to afford 1.4 g of solids. The solids were subjected to preparative TLC on silica gel using benzene-hexane (3 : 5) as solvent to afford two products, **2a** and 9-(4-ethoxyphenyl)-9-(pentadeuteriophenyl) thioxanthene (**6**) as colorless plates from ethanol-dichloromethane, mp 174℃, IR (KBr) cm^{-1} : 2240 (C-D). ^1H-NMR ($CDCl_3$) δ : 1.40 (3H, t, J= 7 Hz, CH_2CH_3), 4.05 (2H, q, J= 7 Hz, CH_2CH_3), 6.72-7.52 (12H, m, ArH). MS$m/z$: 399 (M^+). *Anal.* Calcd for $C_{27}H_{17}D_5OS$: C, 81.17 ; H, 6.81. Found : C, 81.09 ; H, 7.02. In the mass spectrum of the crude reaction products, no molecular ion peaks (m/z 394 or 385) corresponding to the crossed products could be observed.

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