quantity, retention time, 31.78 min at 50 °C. *cis,cis*-2,4-Hexadiene was not in our possession.

Reaction of *trans,trans*-2,4-Hexadiene with [Hydroxy(tosyloxy)iodo]benzene. To a mixture of 1 (8.00 g, 20.4 mmol) and CH_2Cl_2 (~50 mL), cooled to 3 °C, was added a solution of *trans,trans*-2,4-hexadiene (2.167 g, 26.4 mmol) in CH_2Cl_2 (~5 mL); an additional 5 mL of CH_2Cl_2 was used for rinsing purposes and added to the reaction mixture (temperature after mixing, ~4.5 °C). The reaction mixture was stirred for 1 h at ice-bath temperature and allowed to stand for ca. 1 day at 0–1 °C. A straw colored solution mixed with some crystals of *p*-toluenesulfonic acid resulted. This was extracted with H_2O (2 × 35 mL), dried (Na_2SO_4), and concentrated, under aspirator vacuum, to a light brown slush. Trituration of the slush with Et_2O left a white, crystalline solid which was isolated, washed with Et_2O, and identified as 2,5-bis(tosyloxy)-3-hexene: yield, 1.509 g (34.9%); mp 75–76 °C (rapid decomposition to black tar, darkening at 72 °C); ^1H NMR (CD_2Cl_2) δ 1.18 (d, 5.8 H), 2.41 (s, 5.8 H), 4.58–5.14 (complex m, 2.0 H), 5.23–5.49 (complex, well resolved m centered at ~5.35, 2.3 H), 7.48 (AA'XX' m, 8.2 H).

Thermal Decomposition of 2,3-Dimethyl-2,3-bis(tosyloxy)butane. 1. Solid State. 2,3-Dimethyl-2,3-bis(tosyloxy)-butane (0.334 g, 0.783 mmol) was allowed to stand for 15 days in the dark at room temperature. Decomposition to a black tar occurred within 10 days. The tar was mixed with CH_2Cl_2 (15 mL), and the resulting solution/slurry was extracted with H_2O (2 × 20 mL). The aqueous extracts were combined and titrated with standard aqueous NaOH; the yield of *p*-TsOH was 96%. The CH_2Cl_2 solution was dried (Na_2SO_4), treated with charcoal, and concentrated, under aspirator vacuum, to a yellow oil, the ^1H NMR spectrum of which exhibits only a complex pattern in the aliphatic region.

2. In CH_2Cl_2. A solution of 2,3-dimethyl-2,3-bis(tosyloxy)-butane (0.368 g, 0.863 mmol) in CH_2Cl_2 (10 mL) was allowed to stand for 15 days in the dark at room temperature. Within 7 days, the originally clear solution had turned into a reddish-black mixture. The reaction mixture was extracted with H_2O (2 × 25 mL). The aqueous extracts were combined and titrated with standard, aqueous NaOH; the yield of *p*-TsOH was 1.65 mmol (96%). The CH_2Cl_2 solution was dried (Na_2SO_4), treated with charcoal, and concentrated, under aspirator vacuum, to a yellow oil, the ^1H NMR spectrum of which exhibits only a complex pattern in the aliphatic region.

Reaction of Cyclohexene with [Methoxy(tosyloxy)iodo]-benzene. A solution of [methoxy(tosyloxy)iodo]benzene (2.42 g, 5.96 mmol) and cyclohexene (3.5 mL, 2.8 g, 34 mmol) in CH_2Cl_2 (15 mL) was allowed to stand for 3 days at room temperature and subsequently concentrated, under aspirator vacuum, to an oil. The oil was dissolved in Et_2O (10 mL), and the resulting solution was cooled at 0 °C to give 0.91 g of crude *cis*-1,2-bis(tosyloxy)-cyclohexane. Concentration of the mother liquor, dissolution of the residual oil in pentane (10 mL), and cooling at −20 °C gave 0.09 g more of product: combined yield, 1.00 g (79%); clean by ^1H NMR assay. Recrystallization of the crude product from Et_2O (10 mL)/CH_2Cl_2 (a few drops) returned two fractions: 0.74 g (mp 115–117 °C); 0.064 g (mp 114–117 °C, obtained at −20 °C).

Registry No. *dl*-**1**, 27126-76-7; *dl*-**1** (*p*-chloro derivative), 73178-07-1; *dl*-**1** (*o*-methyl derivative), 73177-97-6; *dl*-**1** (methoxy derivative), 75067-08-2; *meso*-**2** ($R_1 = R_2 = Me$, $R_3 = R_4 = H$), 90026-01-0; *meso*-**2** ($R_1 = R_2 = Me$, $R_3 = R_4 = H$, diol), 5341-95-7; *dl*-**2** ($R_1 = R_3 = Me$, $R_2 = R_4 = H$), 90026-02-1; **2** ($R_1 = R_4 = Me$, $R_2 = R_3 = H$), 89959-72-8; *dl-erythro*-**2** ($R_1 = Me$, $R_2 = Et$, $R_3 = R_4 = H$), 89959-73-9; *dl-erythro*-**2** ($R_1 = Me$, $R_2 = Et$, $R_3 = R_4 = H$, diol), 61828-35-1; *dl-threo*-**2** ($R_1 = Me$, $R_3 = Et$, $R_2 = R_4 = H$), 89959-74-0; *dl-threo*-**2** ($R_1 = Me$, $R_3 = Et$, $R_2 = R_4 = H$, diol), 61828-36-2; *dl*-**2** ($R_1 = n$-Pr, $R_2 = R_3 = R_4 = H$), 89959-76-2; *meso*-**2** ($R_1 = R_2 = Et$, $R_3 = R_4 = H$), 89959-77-3; *meso*-**2** ($R_1 = R_2 = Et$, $R_3 = R_4 = H$, diol), 22520-39-4; *dl*-**2** ($R_1 = R_3 = Et$, $R_2 = R_4 = H$, diol), 22520-19-0; *meso*-**2** ($R_1 = R_2 = n$-Pr, $R_3 = R_4 = H$), 89959-78-4; *meso*-**2** ($R_1 = R_2 = n$-Pr, $R_3 = R_4 = H$, diol), 22520-41-8; *dl*-**2** ($R_1 = R_3 = n$-Pr, $R_2 = R_4 = H$, diol), 22520-40-7; **2** ($R_1 = R_2 = R_3 = R_4 = Me$), 79069-18-4; *dl*-**2** ($R_1 = Ph$, $R_2 = R_3 = R_4 = H$), 90026-03-2; *meso*-**2** ($R_1 = R_2 = Ph$, $R_3 = R_4 = H$), 36439-55-1; *meso*-**2** ($R_1 = R_2 = Ph$, $R_3 = R_4 = H$, diol), 579-43-1; *dl*-**2** ($R_1 = R_3 = Ph$, $R_2 = R_4 = H$), 36528-58-2; *dl*-**2** ($R_1 = R_3 = Ph$, $R_2 = R_4 = H$, diol), 655-48-1; **4**, 89959-82-0; **5**, 89959-81-9; **7**, 89959-80-8; **8**, 89959-79-5; (*Z*)-MeCH=CHMe, 590-18-1; (*E*)-MeCH=CHMe, 624-64-6; $Me_2C=CH_2$, 115-11-7; (*Z*)-MeCH=CHEt, 627-20-3; (*E*)-MeCH=CHEt, 646-04-8; *n*-PrCH=CH_2, 109-67-1; (*Z*)-EtCH=CHEt, 7642-09-3; (*E*)-EtCH=CHEt, 13269-52-8; (*Z*)-*n*-PrCH=CHPr-*n*, 7642-15-1; (*E*)-*n*-PrCH=CHPr-*n*, 14850-23-8; $Me_2C=CMe_2$, 563-79-1; PhCH=CH_2, 100-42-5; (*Z*)-PhCH=CHPh, 645-49-8; (*E*)-PhCH=CHPh, 103-30-0; $Ph_2C=CH_2$, 530-48-3; (*E,E*)-MeCH=CHCH=CHMe, 5194-51-4; (*E,Z*)-MeCH=CHCH=CHMe, 5194-50-3; $Ph_2C=CH\text{-}I^+\text{-}Ph\ ^-OTs$, 79069-21-9; *cis*-1,2-cyclohexanediol ditosylate, 5433-22-7; *cis*-1,2-cyclohexanediol, 1792-81-0; *dl-trans*-1,2-cyclohexanediol ditosylate, 89959-86-4; *dl-trans*-1,2-cyclohexanediol, 54383-22-1; *dl-trans*-1-hydroxy-2-(tosyloxy)cyclohexane, 89959-75-1; 1,2-diphenyl-2,3-bis(tosyloxy)-1-oxopropane, 89959-83-1; 1,1-bis(tosyloxy)-2-phenylethane, 79069-22-0; deoxybenzoin, 451-40-1; 2,7-bis(tosyloxy)norbornane, 89959-84-2; 2,3-bis(tosyloxy)norbornane, 89959-85-3; cyclopentene, 142-29-0; cyclohexene, 110-83-8; methylenecyclopentane, 1528-30-9; chalcone, 94-41-7; norbornene, 498-66-8; *cis*-4-octene oxide, 1439-06-1; cyclohexene oxide, 286-20-4.

Supplementary Material Available: Experimental details for the preparation of *vic*-bis(tosyloxy)alkanes from alkenes and PhI(OH)OTs; NMR data for *vic*-bis(tosyloxy)alkanes (13 pages). Ordering information is given on any current masthead page.

Novel Rearrangement of 1,4-Ylidic Thiaanthracenes

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A novel rearrangement of 10-alkyl-9-aryl-10-thiaanthracenes is described. 9-Mesityl-10-methyl-10-thiaanthracene (**8a**) generated by proton abstraction of 9-mesityl-10-methylthioxanthenium perchlorate (**7a**) with sodium hydride in THF underwent thermal rearrangement to afford 3-methyl-9-mesitylthioxanthene (**9a**). Similarly, the 9-bulky aryl group substituted 10-alkyl-10-thiaanthracenes **7b–f** were decomposed thermally to give the corresponding 3-alkyl-9-arylthioxanthenes **9b–f** in 63–67% isolated yields. It is discussed that these abnormal alkyl rearrangements were caused by the steric effect of the bulky substituents at the 9-position of the thiaanthracenes, which prevent the normal 1,4-sigmatropic rearrangement of the 10-alkyl group to the 9-position.

It is reported[1] that 9,10-disubstituted 10-thiaanthracenes **2a**, which are generated by treatment of the corresponding thioxanthenium salts **1a** with base, undergo thermal six-electron 1,4-rearrangement of 10-substituents to give the

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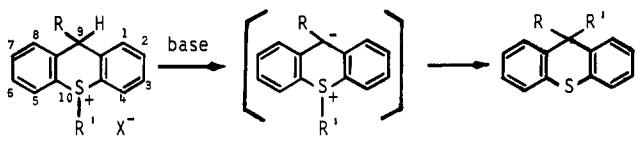
Table I. ^{1}H NMR Spectral Data for 3-Alkyl-9-arylthioxanthenes (9) and 3-Alkyl-9-arylthioxanthene 10,10-Dioxides (10) in $CDCl_3$[a]

compd	H-1	H-2	compd	R^1	R^2	H-1	H-2
9a	6.69 (d, J = 8.6 Hz)[b]						
9b	6.72 (d, J = 8.7 Hz)		**10b**	Mes	Et	6.89 (d, J = 8.3 Hz)	8.11 (d, J = 1.6 Hz)
9c	6.71 (d, J = 8.3 Hz)		**10c**	Mes	Pr	6.88 (d, J = 8.3 Hz)	8.08 (d, J = 1.5 Hz)
9d	6.60 (d, J = 8.8 Hz)						
9e	6.69 (d, J = 7.8 Hz)	6.90 (dd, J = 7.8, 1.6 Hz)[c]					
9f	6.62 (d, J = 8.7 Hz)	6.82 (dd, J = 8.7, 1.3 Hz)	**10f**	Dur	Pr	6.88 (d, J = 8.0 Hz)	8.13 (d, J = 1.9 Hz)

[a] Chemical shifts are reported in ppm downfield from Me_4Si. [b] d: doublet. [c] dd: doublet of doublets.

corresponding 9,9-disubstituted thioxanthenes **3a**, in an excellent yield. Furthermore, we recently reported[2] the



1 2 3

a, R = H, Me, aryl
R′ = alkyl, aryl
b, R = CN, CO_2Et
R′ = Me

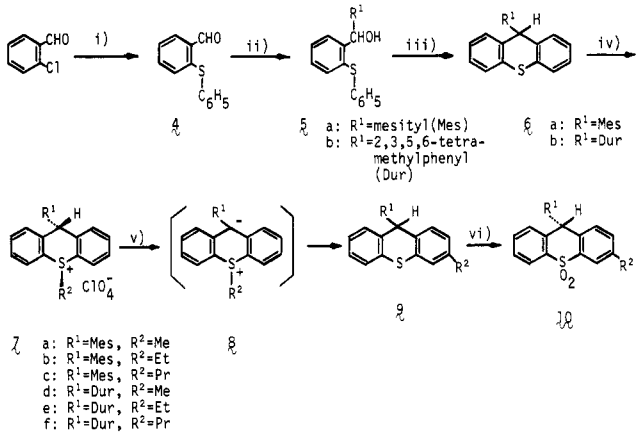
first synthesis of stable thiaanthracenes **2b**, in which ylidic carbanion electrons were delocalized toward the electron-withdrawing cyano or ethoxycarbonyl group at the 9-position. However, these stable thiaanthracenes also underwent thermal 1,4-rearrangement to produce the corresponding thioxanthenes **3b** on heating. It appeared to be of interest to investigate the stabilities of the new type of 9,10-disubstituted 10-thiaanthracenes having sterically hindered substituents at the 9-position which may play an effective role in preventing the 10-alkyl substituents from rearranging to the 9-position of the thiaanthracene.

This paper presents the details of the new rearrangement reaction of 10-alkyl-9-(2,4,6-trimethylphenyl)- and 10-alkyl-(2,3,5,6-tetramethylphenyl)-10-thiaanthracenes.[3]

Results and Discussion

Reaction of 2-(phenylthio)benzaldehyde (**4**)[4] with 2,4,6-trimethylphenyl- (mesityl) or 2,3,5,6-tetramethylphenyl- (duryl) magnesium bromide followed by cyclization with 80% sulfuric acid afforded 9-mesitylthioxanthene (**6a**) or 9-durylthioxanthene (**6b**) in 95% or 91% yield, respectively. Alkylation of the thioxanthenes **6a,b** with alkyl halides in the presence of silver perchlorate in 1,2-dichloroethane gave the corresponding 10-alkyl-9-arylthioxanthenium perchlorates **7a–f** in high yields. All the thioxanthenium salts **7** exist in a trans configuration as shown in Scheme I, which was established by the detailed studies of ^{1}H NMR spectral data.[5,6]

Scheme I[a]



[a] Reagents: i, benzenethiol, Na_2CO_3, HMPA; ii, R^1MgBr, ether; iii, 80% H_2SO_4; iv, R^2I, $AgClO_4$, $ClCH_2CH_2Cl$; v, NaH, THF; vi, *m*-chloroperbenzoic acid, CH_2Cl_2.

Treatment of the thioxanthenium salts **7** with sodium hydride in tetrahydrofuran (THF) under nitrogen atmosphere at room temperature yielded an orange-yellow solution of 1,4-ylides **8**. After the orange-yellow color changed to dark brown, the rearranged products, 3-alkyl-9-arylthioxanthenes **9**, were obtained in 63–68% isolated yields.

The structure of **9**, especially the orientation of the rearranged alkyl group, was assigned on the basis of ^{1}H NMR spectral data (Table I) and chemical conversion of some of **9** to the corresponding sulfones **10**. In the ^{1}H NMR of **9**, the doublet signal (J = 7.8–8.8 Hz) of the H-2 of the thioxanthene ring appears at δ 6.60–6.72. The doublet is due to ortho coupling with H-2 of the thioxanthene ring. Although the signals of H-2 of **9a**, **9b**, **9c**, and **9d** overlap with other aromatic protons, and hence are not clearly assigned, the ^{1}H NMR spectra of **9e** and **9f** showed the clear coupling feature of H-2, which consists of ortho coupling (J = 7.8, 8.7 Hz, respectively) with H-1 and meta coupling (J = 1.6, 1.3 Hz, respectively) with H-4. The thioxanthenes **9b,c,f** were oxidized by *m*-chloroperbenzoic acid to the corresponding 3-alkyl-9-arylthioxanthene 10,10-dioxides **10b,c,f**.[7] In the ^{1}H NMR spectra of the sulfones **10b,c,f**, H-4 of the thioxanthene ring is highly shifted downfield by the effect of an *o*-sulfonyl group and

(1) (a) Hori, M.; Kataoka, T.; Shimizu, H.; Hsü, C. F. *Chem. Lett.* **1973**, 391. (b) Hori, M.; Kataoka, T.; Shimizu, H. *Ibid.* **1974**, 1117. (c) Senkler, Jr., G. H.; Stackhouse, J.; Maryanoff, B. E.; Mislow, K. *J. Am. Chem. Soc.* **1974**, *96*, 5648. (d) Ogura, F.; Hounshell, W. D.; Maryanoff, C. A.; Richter, W. J.; Mislow, K. *Ibid.* **1976**, *98*, 3615. (e) Pirelahi, H.; Abdoh, Y.; Afzali, A. *Tetrahedron Lett.* **1976**, 4609. (f) Maryanoff, C. A.; Hayes, K. S.; Mislow, K. *J. Am. Chem. Soc.* **1977**, *99*, 4412.

(2) (a) Hori, M.; Kataoka, T.; Shimizu, H.; Ohno, S.; Narita, K. *Tetrahedron Lett.* **1978**, 251. (b) Hori, M.; Kataoka, T.; Shimizu, H.; Ohno, S. *Heterocycles* **1977**, *7*, 863. (c) Hori, M.; Kataoka, T.; Shimizu, H.; Ohno, S. *J. Org. Chem.* **1980**, *45*, 2468.

(3) A preliminary communication of part of this work has been published: Hori, M.; Kataoka, T.; Shimizu, H.; Ohno, S. *Tetrahedron Lett.* **1978**, 255.

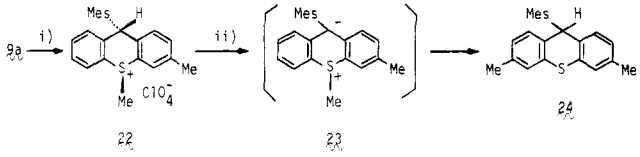
(4) Jacques, G. Ger. Patent 2165260, 1972; *Chem. Abstr.* **1972**, *77*, 114271j).

(5) The determination of the stereochemistry of many 10-alkyl-9-arylthioxanthenium salts we have synthesized has been already reported.[6] Signals based on the methyl groups at pseudoaxial and pseudoequatorial positions appear in higher field than δ 3.39 and in lower field than δ 3.48, respectively, in the ^{1}H NMR spectra in CF_3CO_2H. A full detailed report will be published in the near future.

(6) Hori, M.; Kataoka, T.; Shimizu, H.; Ohno, S. *Heterocycles* **1979**, *12*, 1555.

(7) It has been confirmed that the 9-aryl group of **10** occupies a pseudoequatorial position: Hori, M.; Kataoka, T.; Shimizu, H.; Ohno, S. *Heterocycles* **1979**, *12*, 1417.

Scheme II[a]



[a] Reagents: i, MeI, $AgClO_4$, $ClCH_2CH_2Cl$; ii, NaH, THF.

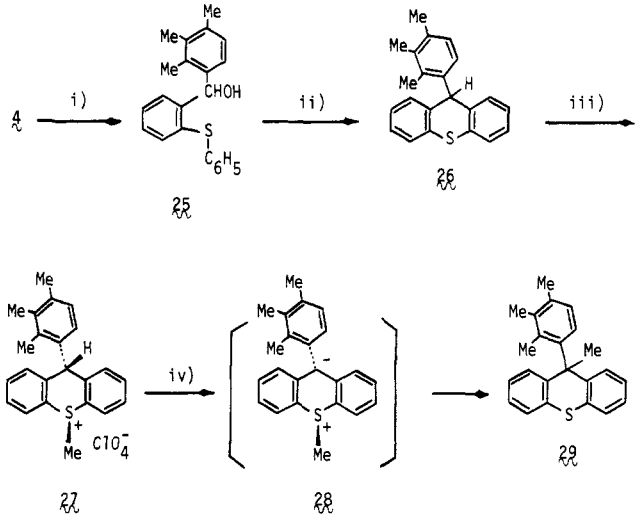
meta coupling (J = 1.5–1.9 Hz) with H-2 was clearly observed, but with no ortho coupling, as shown in Table I. In addition, the H-1 signals of the sulfones are observed at δ 6.88–6.89 as a doublet (J = 8.0–8.3 Hz) due to the ortho coupling with H-2. From these ^1H NMR spectral data, it is evident that the rearranged alkyl group is located at the 3-position of the thioxanthene ring.

The structures of the rearranged products **9** were further confirmed by an independent synthesis of the samples. Reaction of 2-bromo-4-methylbenzaldehyde (**11**)[8] with benzenethiol in the presence of sodium carbonate afforded 4-methyl-2-(phenylthio)benzaldehyde (**12**), which was subjected to the Grignard reaction with mesitylmagnesium bromide to yield mesityl[4-methyl-2-(phenylthio)phenyl]methanol (**13**). Mesitylmethanol **13** was treated with 80% sulfuric acid to give **9a** in 89% yield. Compound **9a** was also prepared from 2-bromo-4-methylaniline (**14**).[9] Diazotization of **14** followed by addition of KCN afforded 2-bromo-4-methylbenzonitrile (**15**). Reaction of **15** with benzenethiol in HMPA gave 4-methyl-2-(phenylthio)-benzonitrile (**16**) in 87% yield, which was hydrolyzed to 4-methyl-2-(phenylthio)benzoic acid (**17**). Acid **17** was easily cyclized with PPA to give 3-methylthioxanthone (**18**) in 90% yield. Reduction of **18** with sodium borohydride, followed by treatment with 70% perchloric acid, yielded 3-methylthioxanthylium perchlorate (**19**) in 72% yield. Treatment of **19** with mesitylmagnesium bromide produced **9a** in 69% yield. Similarly, on treatment of **19** with durylmagnesium bromide, **9d** was prepared in 67% yield. Compound **9d** was also prepared by cyclization of duryl-[2-[(3-methylphenyl)thio]phenyl]methanol (**21**) with 80% sulfuric acid which was synthesized by the reaction of 2-chlorobenzaldehyde with 3-methylbenzenethiol, followed by Grignard reaction with durylmagnesium bromide. In this cyclization reaction of **21**, there are two possible reaction sites, the 2- and 6-positions on the tolyl group. However, only one product, formed by cyclization at the 6-position of the tolyl ring was obtained, presumably because the 2-position is highly hindered by steric repulsion between the methyls in the tolyl and duryl rings.

Thus, it was established that the rearrangement of the 10-alkyl group in these new types of 10-thiaanthracenes occurred to the 3-position of the thioxanthene ring, indicating the anomalous 1,4-rearrangement of 10-thiaanthracenes which have never been observed before.

The thioxanthene **9a** was methylated with methyl iodide in the presence of silver perchlorate to give 3,10-dimethyl-9-mesitylthioxanthenium perchlorate (**22**) whose stereochemistry was determined as the trans configuration as depicted in Scheme II by ^1H NMR studies.[10] Deprotonation of **22** with NaH in THF afforded the rearranged product, 3,6-dimethyl-9-mesitylthioxanthene (**24**) which

Scheme III[a]



[a] Reagents: i, (2,3,4-trimethylphenyl)magnesium bromide; ii, 80% H_2SO_4; iii, MeI, $AgClO_4$, $ClCH_2CH_2Cl$; iv, NaH, THF.

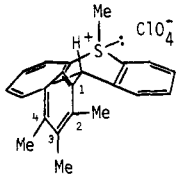


Figure 1. Conformation of 10-methyl-9-(2,3,4-trimethylphenyl)thioxanthenium perchlorate (**27**).

is assumed to be formed by 1,4-migration of the 10-methyl group of the generated thiaanthracene **23** to another possible reaction site, position 5 of the thioxanthene ring. The structure of **24** is evident from the ^1H NMR spectral data, showing doublet signals (J = 8.1 Hz) at δ 6.61 due to two equivalent protons of H-1 and H-8, doublets of doublet signals (J = 8.1 and 1.2 Hz) at δ 6.79 assigned to H-2 and H-7, and a doublet signal (J = 1.2 Hz) attributable to H-4 and H-5.

In order to get more information on the steric effect of the 9-aryl group for this new rearrangement, we have carried out the rearrangement of the 10-methyl-9-(2,3,4-trimethylphenyl)-10-thiaanthracene (**28**) (Scheme III). The precursor of **28**, 10-methyl-9-(2,3,4-trimethylphenyl)thioxanthenium perchlorate (**27**)[5,6] was prepared by a method similar to the case of **7**. Treatment of **27** with NaH in THF generated the thiaanthracene **28** as an orange-yellow solution, which underwent a normal six-electron, 1,4-sigmatropic rearrangement to result in the formation of 9-methyl-9-(2,3,4-trimethylphenyl)thioxanthene (**29**). The structure of **29** is apparent from the ^1H NMR spectrum showing the absence of a H-9 signal. Instead a 9-Me signal was observed at δ 1.78.

This normal methyl migration indicates that a 2,3,4-trimethylphenyl group at the 9-position played no effective role for blocking the migration of the 10-methyl group to the 9-position.

This result might be explained by the conformation of the 2,3,4-trimethylphenyl group at the 9-position of thiaanthracene **28** which is considered to be almost similar to that of the thioxanthenium salt **27**. In the ^1H NMR spectrum of **27**, the 2-methyl group of the 9-aryl substituent appeared at significantly high field (δ 1.53), caused by the strong anisotropy of the aromatic ring of the thioxanthene, indicating that the orientation of the 2-methyl group was just under the thioxanthene ring as shown in

(8) Jolad, S. D.; Rajagpal, S. "Organic Syntheses"; Corey, E. J., Ed.; Wiley: New York: 1966; Vol. 46, p 13.
(9) Johnson, J. R.; Sandborn, L. T. "Organic Syntheses"; Gilman, H., Ed.; Wiley: New York: 1956; Collect. Vol. 1, p 111.
(10) Together with **22** (trans form), a trace amount of cis isomer was formed simultaneously, whose structure was confirmed by the ^1H NMR spectrum showing a 10-methyl signal at δ 3.60 in CF_3CO_2H, indicating pseudoequatorial conformation of the methyl group.[5]

Scheme IV

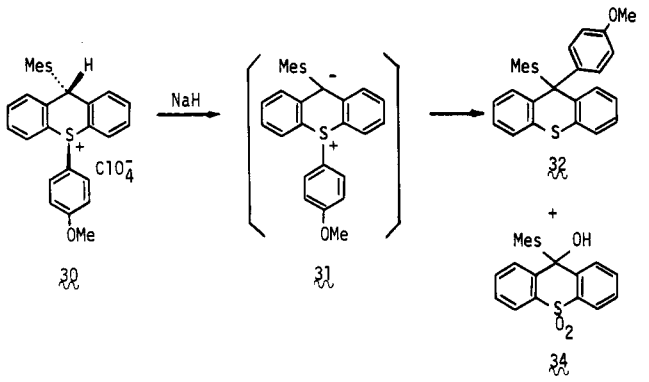


Figure 1. Hence no hindrance exists at the 9-position to prevent the migration of the methyl group.

We next investigated the rearrangement of 10-arylthiaanthracenes having a bulky group at the 9-position (Scheme IV). For example, treatment of 9-mesityl-10-(*p*-methoxyphenyl)thioxanthenium perchlorate (**30**) with NaH in THF under nitrogen atmosphere generated a deep red solution of 9-mesityl-10-(*p*-methoxyphenyl)-10-thiaanthracene (**31**). The deep red color was unchanged even when the solution was kept at room temperature for 15 h, but on refluxing for 2 h the color disappeared, resulting in the formation of the six-electron 1,4-sigmatropic rearranged product, 9-mesityl-9-(*p*-methoxyphenyl)thioxanthene (**32**) in 39% isolated yield. The thiaanthracene **31** is quite stable in solution in comparison with 10-(*p*-methoxyphenyl)-9-phenyl-10-thiaanthracene which was generated from the corresponding thioxanthenium perchlorate and rapidly converted to 9-(*p*-methoxyphenyl)-9-phenylthioxanthene even at room temperature.[1b] In addition to the product **32**, 9-hydroxy-9-mesitylthioxanthene 10,10-dioxide (**34**), **8a**, and unidentified product having an empirical formula of $C_{29}H_{26}O_3S$ (**33**) were isolated in 8%, 6.6%, and 13% yields, respectively. The product **34** seems to be formed by an autoxidation during silica gel workup. The thermostability of **31** would be dependent on the steric hindrance of the 9-substituent, migration of 10-aryl group being prevented.

A significant difference in the rearrangement reaction between 10-alkyl- and 10-aryl-10-thiaanthracenes was observed. A plausible explanation is not clear at the present. Further work is planned to determine their mechanistic implications.

The thioxanthenium salt **30**[11] was synthesized from the reaction of 9-mesitylthioxanthene 10-oxide (**35a**)[12] with anisole in concentrated sulfuric acid, followed by treatment with 70% perchloric acid in 30% yield. In this case, 9-mesitylthioxanthylium perchlorate (**36a**) was also obtained in 45% yield. Interestingly, in the case of 9-durylthioxanthene 10-oxide (**35b**)[12] the corresponding thioxanthenium salt could not be obtained. Only 9-durylthioxanthylium perchlorate (**36b**) was formed in 73% yield under the same conditions.

(11) The configuration of **30** was determined as trans as depicted in Scheme IV on the basis of ^1H NMR spectroscopic studies which were effectively used for the determination of the stereostructure of many 10-alkyl-9-arylthioxanthenium salts.[6] Especially, the conformation of the 10-*p*-methoxyphenyl group was determined to be the pseudoaxial position by the ^1H NMR spectrum which shows the signal of all of the benzene protons of the 10-*p*-methoxyphenyl group at δ 7.26 as a singlet. When the 2,6-protons of the 10-*p*-methoxyphenyl group are located over the two benzene rings of thioxanthene (namely they occupy a pseudoaxial position), they are strongly deshielded by the anisotropic effect of the two benzene rings. Consequently, the signal of the 2,6-protons is observed at the high field, and incidentally, appears at the same field as that of two other aromatic protons (3,5-protons) of the *p*-methoxyphenyl group, showing a singlet.

(12) It has been reported that the sulfoxides **35a** and **35b** exist in trans form.[7]

Experimental Section

Melting points were determined by using a Yanagimoto micromelting point apparatus and are uncorrected. Elemental analyses were performed at the Microanalytical Laboratory of Gifu College of Pharmacy. ^1H nuclear magnetic resonance (^1H NMR) spectra were run on a Hitachi R-20B spectrometer. Chemical shifts are reported in δ units (parts per million downfield from tetramethylsilane). Splitting patterns are designated as follows: s, singlet; d, doublet; t, triplet; q, quartet; br, broad. Coupling constants are given in hertz. Infrared (IR) spectra were determined on a JASCO Model IR A-1 infrared spectrometer. Mass (MS) spectra were recorded with a JEOL JMSD-300 spectrometer at an ionizing voltage of 70 eV. Analytical and preparative thin-layer chromatography were performed by using E. M. Merk silica gel 60PF-254.

2-(Phenylthio)benzaldehyde (4). A mixture of 2-chlorobenzaldehyde (5 g), benzenethiol (5 g), Na_2CO_3 (7 g), and hexamethylphosphoramide (HMPA) (10 mL) was stirred for 5 h at 80–90 °C. After cooling, the reaction mixture was poured into water and extracted with ether. The extract was washed with water, dried over anhydrous $MgSO_4$, and concentrated to afford an oil which was crystallized by adding hexane to give 7.70 g (90%) of **4**. Recrystallization from hexane gave colorless prisms: mp 47–48 °C (lit.[4] mp 50–51 °C); IR (KBr) 2740 (CHO), 1692 and 1673 cm^{-1} (CO); ^1H NMR ($CDCl_3$) δ 7.04–7.06 (m, Ar H), 7.84–8.04 (m, H-6), 10.47 (s, CHO). Anal. Calcd for $C_{13}H_{10}OS$: C, 72.87; H, 4.70. Found: C, 72.61; H, 4.60.

The 2-(arylthio)benzaldehyde derivatives **12** and **20** were prepared following the procedure as given for **4** from the corresponding 2-halobenzaldehydes and benzenethiols. See the paragraph at the end of the paper about supplementary material concerning the characteristics of the compounds **12** and **20**.

Mesityl[2-(phenylthio)phenyl]methanol (5a). To a solution of Grignard reagent, prepared from mesityl bromide (13 g), Mg (1.6 g), ether (50 mL), and catalytic amounts of I_2 was added dropwise a solution of **4** (10 g) in ether (50 mL). The mixture was refluxed for 3 h and then treated with an NH_4Cl solution. The organic layer was separated, washed with water, and dried over anhydrous $MgSO_4$. Removal of the solvent gave an oil, which was purified by column chromatography on silica gel using CH_2Cl_2–petroleum ether (1:1) to afford 14 g (90%) of **5a** as colorless oil: bp 200 °C (0.1 mmHg, bath temperature); IR (neat) 3390 cm^{-1} (OH); ^1H NMR ($CDCl_3$) δ 2.21 (s, 2- and 6-Me of mesityl group), 2.28 (s, 4-Me of mesityl group), 2.82 (d, J = 3.6 Hz, OH), 6.46 (d, J = 3.6 Hz, C*H*OH), 6.87 (s, H-3 and H-5 of mesityl group), 7.10–7.50 (m, Ar H). Anal. Calcd for $C_{22}H_{22}OS$: C, 79.00; H, 6.63. Found: C, 79.01; H, 6.59.

The methanol derivatives **5b**, **13**, **21**, and **25** were prepared following the procedure as given for **5a** from the reaction of the corresponding 2-(arylthio)benzaldehydes and Grignard reagents. See the paragraph at the end of the paper about supplementary material concerning the characteristics of the compounds **5b**, **13**, **21**, and **25**.

9-Mesitylthioxanthene (6a). A mixture of **5a** (10 g) and 80% H_2SO_4 (50 mL) was heated on a water bath for 30 min with occasional shaking. The reaction mixture was poured into cold water and extracted with CH_2Cl_2. The extract was washed with water, dried over silica gel, and concentrated to give crystals. Recrystallization from CH_2Cl_2–MeOH gave 9 g (95%) of **6a** as colorless scales: mp 156–158 °C (lit.[13] mp 155–157 °C); ^1H NMR ($CDCl_3$) δ 2.06 (s, 2- and 6-Me of mesityl group), 2.39 (s, 4-Me of mesityl group), 5.42 (br s, H-9), 6.69–7.56 (m, ArH). Anal. Calcd for $C_{22}H_{20}S$: C, 83.50; H, 6.37. Found: C, 83.71; H, 6.35.

The 9-arylthioxanthenes **6b**, **9a**, **9d**, and **26** were prepared following the procedure as given for **6a** from the corresponding methanol derivatives **5b**, **13**, **21**, and **25**. See the paragraph at the end of the paper about supplementary material concerning the characteristics of the compounds **6b**, **9a**, **9d**, and **26**.

(13) Maryanoff, B. E.; Stackhouse, J.; Senkler, Jr., G. H.; Mislow, K. *J. Am. Chem. Soc.* **1975**, *97*, 2718.

10-Alkyl-9-arylthioxanthenium Perchlorates 7. 7a: To a solution of **6a** (1 g) and methyl iodide (5 g) in 1,2-dichloroethane (10 mL) was added silver perchlorate (0.8 g) and the mixture was stirred overnight. The precipitate was filtered off and washed with hot acetone. The filtrate was concentrated to ca. 10 mL in vacuo and diluted with ether to afford 1.28 g (94%) of **7a**. Recrystallization from CH_2Cl_2–ether gave colorless needles: mp 209–216 °C dec; ^1H NMR (CF_3CO_2H) δ 1.29 (br, $W_{1/2}$ = 0.14 ppm, 6-Me of mesityl group), 2,44 (s, 4-Me of mesityl group), 2.60 (br, $W_{1/2}$ = 0.11 ppm, 2-Me of mesityl group), 3.29 (s, 10-Me), 6.20 (br, $W_{1/2}$ = 3.9 Hz, H-9), 6.90–7.57 (m, H-1 and H-2 and H-3 and H-5 of mesityl group), 7.60–8.02 (m, Ar H), 8.02–8.24 (m, H-4 and H-5). Anal. Calcd for $C_{23}H_{23}ClO_4S$: C, 64.10; H, 5.38. Found: C, 63.85; H, 5.17.

In a similar manner as above, other thioxanthenium perchlorates **7b–f** were prepared from **6a** or **6b** and the corresponding alkyl iodides. See the paragraph at the end of the paper about supplementary material concerning the characteristics of the compounds **7b–f**.

Generation of 10-Alkyl-9-aryl-10-thiaanthracenes 8a–f and Their Rearrangement to 3-Alkyl-9-arylthioxanthenes 9a–f. 9a: To a mixture of **7a** (400 mg) and THF (10 mL) was added NaH (50% in oil, 80 mg) under nitrogen atmosphere, yielding an orange-yellow solution of **8a**. After stirring for 3 h, the mixture was poured into cold water and extracted with ether. The extract was washed with water, dried over anhydrous $MgSO_4$, and concentrated in vacuo to afford an oil. The oil was purified by column chromatography on silica gel using CH_2Cl_2–petroleum ether (1:9) to give an oil which soon solidified. Recrystallization from CH_2Cl_2–MeOH gave 241 mg (68%) of **9a** as colorless plates: mp 134–136 °C; ^1H NMR ($CDCl_3$) δ 2.06 (s, 2- and 6-Me of mesityl group), 2.30 (s, 3-Me), 2.39 (s, 4-Me of mesityl group), 5.41 (br s, H-9), 6.69 (d, J = 8.6 Hz, H-1), 6.69–7.56 (m, Ar H). Anal. Calcd for $C_{23}H_{22}S$: C, 83.59; H, 6.71. Found: C, 83.75; H, 6.67.

In a similar manner as above, other thioxanthenes **9b–f** were obtained from **7b–f** by treating with NaH in THF. See the paragraph at the end of the paper about supplementary material concerning the characteristics of the compounds **9b–f**.

Oxidation of 9 to 3-Alkyl-9-arylthioxanthene 10,10-Dioxides 10. 10b: To a solution of **9b** (171 mg) in CH_2Cl_2 (10 mL) was added 85% *m*-chloroperbenzoic acid (210 mg). The mixture was stirred overnight, washed with a Na_2CO_3 solution and then water, and dried over anhydrous $MgSO_4$. Evaporation of the solvent gave an oil which was crystallized with petroleum ether. Recrystallization from CH_2Cl_2–MeOH gave 155 mg (83%) of **10b** as colorless rhombus: mp 201–204 °C; IR (KBr) 1303 and 1158 cm^{-1} (SO_2); ^1H NMR ($CDCl_3$) δ 1.28 (t, J = 7.0 Hz, CH_2CH_3), 1.36 (br s, 6-Me of mesityl group), 2.40 (s, 4-Me of mesityl group), 2.45 (br s, 2-Me of mesityl group), 2.76 (q, J = 7.0 Hz, CH_2CH_3), 5.91 (br s, $W_{1/2}$ = 3.8 Hz, H-9), 6.89 (d, J = 8.3 Hz, H-1), 6.86–7.74 (m, Ar H), 8.11 (d, J = 1.6 Hz, H-4), 8.17–8.40 (m, H-5). Anal. Calcd for $C_{24}H_{24}O_2S$: C, 76.56; H, 6.42. Found: C, 76.40; H, 6.27.

In a similar way as described above, **10c** and **10f** were obtained from **9c** and **9f**, respectively. See the paragraph at the end of the paper about supplementary material concerning the characteristics of the compounds **10c** and **10f**.

3-Methyl-9-mesitylthioxanthene (9a). To a THF solution of mesitylmagnesium bromide prepared from mesityl bromide (1.4 g), Mg (180 mg), THF (10 mL), and catalytic amounts of I_2 were added ether and subsequently **19** (1.0 g) in limited amounts. The mixture was refluxed for 30 min and treated with an NH_4Cl solution. After addition of CH_2Cl_2, the organic layer was separated, washed with water, and dried over $MgSO_4$. Evaporation of the solvent gave the residue which was recrystallized from CH_2Cl_2–MeOH to afford 0.73 g (69%) of **9a** as colorless needles.

2-Bromo-4-methylbenzonitrile (15). According to the procedure for *o*-tolunitrile by Clark and Read,[14] **15** was prepared from 2-bromo-4-methylaniline[9] (**14**, 18.6 g) in the yeild of 49% (9.6 g): colorless oil; bp 150 °C (20 mmHg); IR (neat) 2220 cm^{-1} (CN); ^1H NMR ($CDCl_3$) δ 2.44 (s, Me), 7.29 (dq, J = 7.2 and 1.1 Hz, H-5), 7.54 (br s, H-3), 7.56 (d, J = 7.2 Hz, H-6).

4-Methyl-2-(phenylthio)benzonitrile (16). A mixture of **15** (9.6 g), benzenethiol (10 mL), Na_2CO_3 (10 g), and HMPA (50 mL) was stirred for 5 h at 110 °C under nitrogen atmosphere. Workup as for **4** gave a crude oil, which was purified by column chromatography on silica gel using CH_2Cl_2–petroleum ether (2:5) to give 9.58 g (87%) of **16** as a colorless oil: bp 170 °C (1.0 mmHg, bath temperature); IR (neat) 2238 cm^{-1} (CN); ^1H NMR ($CDCl_3$) δ 2.31 (s, Me), 7.00–7.70 (m, Ar H). Anal. Calcd for $C_{14}H_{11}NS$: C, 74.63; H, 4.92; N, 6.22. Found: C, 74.39; H, 4.89; N, 6.12.

4-Methyl-2-(phenylthio)benzoic Acid (17). A mixture of **16** (8.0 g), NaOH (3 g), and methyl Cellosolve (50 mL) was refluxed for 5 h. The reaction mixture was poured into water, acidified with concentrated HCl, and extracted with ether. The extract was washed with water, dried over anhydrous $MgSO_4$, and concentrated to afford 7.3 g (84%) of **17**. Recrystallization from THF–petroleum ether gave colorless needles: mp 194–196 °C; IR (KBr) 3210–2430 (CO_2H), 1684 cm^{-1} (CO); ^1H NMR ($CDCl_3$) δ 2.21 (s, Me), 6.69 (br s, H-3), 7.04 (br d, J = 7.1 Hz, H-5), 7.40–7.80 (m, Ar H), 8.12 (d, J = 7.1 Hz, H-6), 8.21 (br, COOH). Anal. Calcd for $C_{14}H_{12}O_2S$: C, 68.83; H, 4.95. Found: C, 68.85; H, 4.90.

3-Methylthioxanthone (18). A mixture of **17** (3 g) and polyphosphoric acid prepared from P_2O_5 (25 g) and 85% phosphoric acid (25 g) was stirred at 170 °C for 3 h. The reaction mixture was poured into cold water and extracted with CH_2Cl_2. The extract was washed with a NaOH solution and then water, dried over anhydrous $MgSO_4$, and concentrated to dryness. The residue was recrystallized from CH_2Cl_2–hexane to afford 2.5 g (90%) of **18** as colorless needles: mp 118–120 °C; IR (KBr) 1636 cm^{-1} (CO); ^1H NMR ($CDCl_3$) δ 2.47 (s, Me), 7.20–7.70 (m, Ar H), 8.46–8.80 (m, H-1 and H-8). Anal. Calcd for $C_{14}H_{10}OS$: C, 74.31; H, 4.45. Found: C, 74.21; H, 4.44.

3-Methylthioxanthylium Perchlorate (19). To a suspension of **18** (2.3 g) in MeOH (20 mL) was added $NaBH_4$ (2 g) in limited amounts with stirring and the mixture was refluxed for 1 h. The reaction mixture was poured into cold water and extracted with CH_2Cl_2. The extract was washed with water and dried over anhydrous $MgSO_4$. Removal of the solvent gave an oil, which was dissolved in acetic acid (30 mL) and to this solution was added 70% perchloric acid (2 mL). The mixture was heated for 10 min on a water bath and diluted with ether to precipitate violet needles which were collected and washed sufficiently with ether. Recrystallization from CH_2Cl_2–ether gave 2.26 g (72%) of **19** as violet needles: mp 169–179 °C dec; IR (KBr) 1100 cm^{-1} (ClO_4^-); ^1H NMR (CF_3CO_2H) δ 2.92 (s, Me), 7.95–8.89 (m, Ar H). Anal. Calcd for $C_{14}H_{11}ClO_4S$: C, 54.11; H, 3.57. Found: C, 53.91; H, 3.49.

3,10-Dimethyl-9-mesitylthioxanthenium Perchlorate (22) and Its Stereoisomer (38). To a solution of **9a** (1 g) and methyl iodide (4 g) in 1,2-dichloroethane (30 mL) was added portionwise silver perchlorate (1.2 g) and the mixture was stirred overnight. The precipitate was filtered off and washed with hot acetone. The filtrate was concentrated in vacuo to ca. 10 mL and diluted with ether to afford 1.25 g (93%) of a crystalline mixture of **22** and **38** (the ratio of **22** and **38** was 7 according to ^1H NMR spectrum). Recrystallization of the mixture from CH_2Cl_2–MeOH afforded colorless scales and colorless needles which were separated mechanically.

22: colorless scales; mp 189–193 °C dec; ^1H NMR (CF_3CO_2H) δ 1.27 (br, $W_{1/2}$ = 0.11 ppm, 6-Me of mesityl group), 2.40 (s, 4-Me of mesityl group), 2.52 (br s, 2-Me of mesityl group and 3-Me), 3.23 (s, 10-Me), 6.04 (br s, $W_{1/2}$ = 3.7 Hz, H-9), 6.80–7.75 (m, Ar H), 7.80 (br s, H-4), 7.88–8.10 (m, H-5). Anal. Calcd for $C_{24}H_{25}ClO_4S$: C, 64.78; H, 5.66. Found: C, 64.66; H, 5.56.

38: colorless needles; mp 172–176 °C dec; ^1H NMR (CF_3CO_2H) δ 1.00–2.80 (br, 2- and 6-Me), 2.36 (s, 4-Me of mesityl group), 2.50 (s, 3-Me), 3.60 (s, 10-Me), 5.94 (br s, $W_{1/2}$ = 3.9 Hz, H-9), 6.80–7.92 (m, Ar H). Anal. Calcd for $C_{24}H_{25}ClO_4S$: C, 64.78; H, 5.66. Found: C, 64.59; H, 5.61.

Generation of 3,10-Dimethyl-9-mesityl-10-thiaanthracene (23) and Its Rearrangement to 3,6-Dimethyl-9-mesitylthioxanthene (24). To a suspension of **22** (1.3 g) in THF (20 mL) was added NaH (50% dispersion in oil, 200 mg) under a nitrogen atmosphere, yielding an orange-yellow solution of **23**. The solution was stirred for 10 h, poured into cold water, and extracted with ether. The extract was washed with water, dried over anhydrous $MgSO_4$, and concentrated to dryness. The residual oil was purified by column chromatography on silica gel using CH_2Cl_2–petroleum ether (1:9) to give 773 mg (77%) of crystals which were recrys-

(14) Clarke, H. T.; Read, R. R. "Organic Syntheses" Gilman, H., Ed.; Wiley: New York: 1956; Collect. Vol. 1, p 514.

tallized from CH_2Cl_2–MeOH to form pale yellow rhombus: mp 172–174 °C; ^1H NMR ($CDCl_3$) δ 2.03 (s, 2- and 6-Me of mesityl group), 2.28 (s, 3- and 6-Me), 2.37 (s, 4-Me of mesityl group), 5.34 (br, $W_{1/2}$ = 0.07 ppm, H-9), 6.61 (d, J = 8.1 Hz, H-1 and H-8), 6.79 (dd, J = 8.1 and 1.2 Hz, H-2 and H-7), 6.96 (s, H-3 and H-5 of mesityl group), 7.17 (d, J = 1.2 Hz, H-4 and H-5). Anal. Calcd for $C_{24}H_{24}S$: C, 83.67; H, 7.20. Found: C, 83.80; H, 7.08.

***trans*-10-Methyl-9-(2,3,4-trimethylphenyl)thioxanthenium Perchlorate (27).** In a similar manner as with **7a**, **27** was prepared from **26** (1 g), methyl iodide (5 g), 1,2-dichloroethane (20 mL), and silver perchlorate (915 mg). Recrystallization from CH_2Cl_2–ether gave 1.3 g (96%) of **27** as colorless needles: mp 191–192 °C dec; IR (KBr) 1100 cm^{-1} (ClO_4^-); ^1H NMR (CF_3CO_2H) δ 1.53 (s, 2-Me of trimethylphenyl group), 2.26 (s, 3-Me of trimethylphenyl group), 2.44 (s, 4-Me of trimethylphenyl group), 3.28 (s, 10-Me), 5.66 (br s, H-9), 7.02–7.45 (m, H-1 and H-8, and H-5 and H-6 of trimethylphenyl group), 7.45–7.80 (m, Ar H), 7.82–8.14 (m, H-4 and H-5). Anal. Calcd for $C_{23}H_{23}ClO_4S$: C, 63.85; H, 5.42. Found: C, 63.73; H, 5.37.

In the ^1H NMR spectrum of the crude product, signals corresponding to trace amounts of the cis isomer **39** were observed: ^1H NMR (CF_3CO_2H) δ 2.22, 2.36 and 2.42 (each s, 3 × Me), 3.72 (s, 10-Me), 5.91 (s, H-9).

Generation of 10-Methyl-9-(2,3,4-trimethylphenyl)-10-thiaanthracene (28) and Its Rearrangement to 9-Methyl-9-(2,3,4-trimethylphenyl)thioxanthene (29). To a suspension of **27** (1 g) in THF (10 mL) was added NaH (50% dispersion in oil, 150 mg) under a nitrogen atmosphere. The orange-yellow solution of generated **28** was stirred overnight. The reaction mixture was poured into water and extracted with CH_2Cl_2. The extract was washed with water, dried over anhydrous $MgSO_4$, and concentrated in vacuo to dryness. The residue was subjected to column chromatography on silica gel using CH_2Cl_2–petroleum ether (1:10) to give 453 mg (59%) of **29**. Recrystallization from CH_2Cl_2–MeOH afforded colorless needles: mp 164–166 °C; ^1H NMR ($CDCl_3$) δ 1.42 (s, 2-Me of trimethylphenyl group), 1.78 (s, 9-Me), 2.07 (s, 3-Me of trimethylphenyl group), 2.37 (s, 4-Me of trimethylphenyl group), 6.49–7.40 (m, Ar H), 7.50 (d, J = 8.3 Hz, H-6 of trimethylphenyl group); mass spectrum, m/e (relative intensity) 330 (M^+, 24), 317 (30), 315 (100), 285 (9), 211 (37), 142 (10). Anal. Calcd for $C_{23}H_{22}S \cdot {}^1/_3CH_2Cl_2$: C, 78.11; H, 6.37. Found: C, 78.16; H, 6.35.

9-Arylthioxanthene 10-Oxides (35a and 35b). 35a: To a solution of **6a** (3 g) in CH_2Cl_2 (30 mL) was added 85% *m*-chloroperbenzoic acid (1.7 g) in limited amounts and the mixture was stirred overnight. The reaction mixture was washed with a Na_2CO_3 solution and water and dried over anhydrous $MgSO_4$. After evaporation of the solvent, the residue was recrystallized from CH_2Cl_2–ether to give 2.93 g (93%) of **35a** as colorless scales: mp 162–173 °C dec; IR (KBr) 1060 cm^{-1} (SO); ^1H NMR ($CDCl_3$) δ 1.88 (s, 2- and 6-Me of mesityl group), 2.39 (s, 4-Me of mesityl group), 6.28 (br s, $W_{1/2}$ = 3.8 Hz, H-9), 7.03 (s, H-3 and H-5 of mesityl group), 6.94–7.23 (m, H-1 and H-8), 7.28–7.64 (m, Ar H), 7.90–8.20 (m, H-4 and H-5); ^1H NMR (C_6D_6) δ 1.71 (s, 2- and 6-Me of mesityl group), 2.22 (s, 4-Me of mesityl group), 6.54 (br s, H-9), 6.80–7.40 (m, Ar H), 7.70–7.97 (m, H-4 and H-5). Anal. Calcd for $C_{22}H_{20}OS$: C, 79.48; H, 6.06. Found: C, 79.37; H, 5.99.

35b: In a similar manner as above, **35b** was prepared from **6b** (4 g), CH_2Cl_2 (40 mL), and *m*-chloroperbenzoic acid (2.45 g). Recrystallization from CH_2Cl_2–MeOH gave 3.9 g (94%) of **35b** as colorless prisms: mp 145 °C dec; IR (KBr) 1020 cm^{-1} (SO); ^1H NMR ($CDCl_3$) δ 1.77 (br s, 2- and 6-Me of duryl group), 2.32 (s, 3- and 5-Me of duryl group), 6.43 (br s, $W_{1/2}$ = 2.9 Hz, H-9), 6.92–7.23 (m, H-4 of duryl group and H-1 and H-8), 7.25–7.65 (m, Ar H), 7.91–8.20 (m, H-4 and H-5); ^1H NMR (C_6D_6) δ 1.66 (br s, 2- and 6-Me of duryl group), 2.12 (s, 3- and 5-Me of duryl group), 6.78 (br s, H-9), 6.87–7.34 (m, Ar H), 7.70–7.97 (m, H-4 and H-5). Anal. Calcd for $C_{23}H_{22}OS$: C, 79.73; H, 6.40. Found: C, 79.47; H, 6.41.

9-Mesityl-10-(*p*-methoxyphenyl)thioxanthenium Perchlorate (30). To a mixture of **35a** (2 g) and anisole (10 mL) was added concentrated H_2SO_4 (1.5 mL) and the mixture was vigorously stirred for 10 days. The reaction mixture was washed with ether; to the residue were added 70% perchloric acid (3 mL) and then water, and it was extracted with CH_2Cl_2. The CH_2Cl_2 layer was washed with water, dried over anhydrous $MgSO_4$, and evaporated to dryness. The residue was dissolved in CH_2Cl_2 and diluted with ether to precipitate a mixture of **30** and 9-mesitylthioxanthylium perchlorate (**36a**). The separation of two products was performed by extraction of **36a** from the mixture with MeOH. The extract was diluted with ether to precipitate red needles which were recrystallized from CH_2Cl_2–ether to give 1.1 g (45%) of **36a** as red needles: mp 251–254 °C dec. The residue was recrystallized from MeOH to give 0.94 g (30%) of **30** as pale yellow prisms: mp 205–208 °C dec; IR (KBr) 1110 cm^{-1} (ClO_4^-); ^1H NMR (CF_3CO_2H) δ 1.83 (br, $W_{1/2}$ = 0.41 ppm, 2- and 6-Me of mesityl group), 2.43 (s, 4-Me of mesityl group), 3.96 (s, OMe), 5.73 (br s, $W_{1/2}$ = 2.9 Hz, H-9), 7.05–7.58 (m, H-1 and H-8), 7.18 (br s, H-3 and H-5 of mesityl group), 7.26 (s, C_6H_4OMe), 7.63–8.01 (m, Ar H), 8.10–8.41 (m, H-4 and H-5). Anal. Calcd for $C_{29}H_{27}ClO_5S$: C, 66.59; H, 5.20. Found: C, 66.62; H, 5.25.

Reaction of 35b with Anisole in the Presence of H_2SO_4. In a similar reaction as above, only **36b** was obtained from **35b** in 73% yield. Recrystallization from CH_2Cl_2–ether gave red needles: mp 272–275 °C.

9-Arylthioxanthen-9-ol (37a and 37b). 37a: To a solution of mesitylmagnesium bromide prepared from mesityl bromide (20 g), Mg (2.6 g), THF (120 mL), and catalytic amounts of I_2 was added thioxanthone (10 g) in limited amounts. The mixture was refluxed for 4 h and hydrolyzed with an NH_4Cl solution. The reaction mixture was extracted with CH_2Cl_2, and the organic layer was separated, washed with water, and dried over anhydrous $MgSO_4$. Removal of the solvent gave an oil which was purified by column chromatography on silica gel using CH_2Cl_2. Recrystallization of the residue from CH_2Cl_2–hexane afforded 10.3 g (66%) of **37a** as colorless plates: mp 165–168 °C; IR (KBr) 3560 and 3430 cm^{-1} (OH); ^1H NMR ($CDCl_3$) δ 2.14 (s, 2- and 6-Me of mesityl group), 2.19 (br s, OH), 2.35 (s, 4-Me of mesityl group), 6.96 (br s, H-3 and H-5 of mesityl group), 7.10–7.60 (m, Ar H). Anal. Calcd for $C_{22}H_{20}OS$: C, 79.48; H, 6.06. Found: C, 79.27; H, 6.11.

37b: In a similar manner as above, **37b** was prepared from durylmagnesium bromide prepared from duryl bromide (20 g), Mg (2.4 g), THF (120 mL), I_2 (catalytic amount), and thioxanthone (10 g). The crude product was purified by column chromatography on silica gel using CH_2Cl_2–petroleum ether (1:1). Recrystallization from CH_2Cl_2–hexane gave 8.2 g (50%) of 9-durylthioxanthen-9-ol (**37b**) as colorless prisms: mp 151–153 °C; IR (KBr) 3420 cm^{-1} (OH); ^1H NMR ($CDCl_3$) δ 2.02 (br, $W_{1/2}$ = 0.25 ppm, 2- and 6-Me of duryl group), 2.17 (s, OH), 2.27 (s, 3- and 5-Me of duryl group), 7.02–7.62 (m, Ar H). Anal. Calcd for $C_{23}H_{22}OS$: C, 79.73; H, 6.40. Found: C, 79.70; H, 6.40.

9-Arylthioxanthylium Perchlorates (36a and 36b). Authentic samples were prepared as follows. **36a**: To a mixture of **37a** (9.3 g) and acetic acid (50 mL) was added 70% perchloric acid (3 mL) and the mixture was heated for 30 min on a water bath. After cooling, the reaction mixture was diluted with ether to precipitate 11.2 g (97%) of 9-mesitylthioxanthylium perchlorate (**36a**) as red crystals which was recrystallized from CH_2Cl_2–ether to form red needles: mp 251–254 °C dec; IR (KBr) 1115 cm^{-1} (ClO_4^-); ^1H NMR (CF_3CO_2H) δ 1.81 (s, 2- and 6-Me of mesityl group), 2.59 (s, 4-Me of mesityl group), 7.39 (s, H-3 and H-5 of mesityl group), 8.00–8.96 (m, Ar H). Anal. Calcd for $C_{22}H_{19}ClO_4S$: C, 63.69; H, 4.62. Found: C, 63.76; H, 4.60.

36b: In a similar manner as above, 9-durylthioxanthylium perchlorate (**36b**) was prepared from **37b** (6 g), acetic acid (50 mL), and 70% perchloric acid (3 mL) in 94% yield: red needles; mp 272–275 °C dec; IR (KBr) 1115 cm^{-1} (ClO_4^-); ^1H NMR (CF_3CO_2H) δ 1.73 (s, 2- and 6-Me of duryl group), 2.49 (s, 3- and 5-Me of duryl group), 7.60 (br s, H-4 of duryl group), 8.00–9.12 (m, Ar H). Anal. Calcd for $C_{23}H_{21}ClO_4S$: C, 64.40; H, 4.94. Found: C, 64.25; H, 4.94.

Generation of 9-Mesityl-10-(*p*-methoxyphenyl)-10-thiaanthracene (31) and Its Rearrangement to 9-Mesityl-9-(*p*-methoxyphenyl)thioxanthene (32). Addition of NaH (50% dispersion in oil, 70 mg) to a stirred suspension of **30** (910 mg) in THF (20 mL) under a nitrogen atmosphere gave a deep red solution of **31**. The solution was refluxed for 2 h to change to a dark brown solution which was poured into water and extracted with CH_2Cl_2. The extract was washed with water, dried over anhydrous $MgSO_4$, and concentrated to dryness in vacuo. The residue was purified by column chromatography on silica gel

using CH_2Cl_2–petroleum ether (1:5). The first fraction gave 36 mg (6.6%) of **6a**. The second fraction was concentrated to afford 288 mg (39%) of 9-mesityl-9-(*p*-methoxyphenyl)thioxanthene (**32**) which was recrystallized from CH_2Cl_2–petroleum ether to form colorless prisms: mp 211–213 °C; ^1H NMR ($CDCl_3$) δ 1.51 (s, 2- and 6-Me of mesityl group), 2.32 (s, 4-Me of mesityl group), 3.73 (s, OMe), 6.87 (br s, H-3 and H-5 of mesityl group), 6.68–7.50 (m, Ar H); mass spectrum, *m/e* (relative intensity) 422 (M^+, 65), 407 (M^+ – Me, 9), 315 (100), 303 (100), 259 (11). Anal. Calcd for $C_{29}H_{26}OS$: C, 82.43; H, 6.20. Found: C, 82.14; H, 6.27. The third fraction gave 101 mg (13%) of unidentified product (**33**) as colorless needles after recrystallization from CH_2Cl_2–MeOH: mp 142–143 °C; ^1H NMR ($CDCl_3$) δ 2.22 (s, 4-Me of mesityl group), 2.40 (s, 2- and 6-Me of mesityl group), 3.78 (s, OMe), 6.73–7.49 (m, Ar H); mass spectrum, *m/e* (relative intensity) 454 (M^+, 100), 345 (41), 335 (24), 315 (91), 243 (38), 239 (38), 206 (37). Anal. Calcd for $C_{29}H_{26}O_3S$: C, 76.62; H, 5.76. Found: C, 76.72; H, 5.75. Finally, CH_2Cl_2 was used as a developing solvent to give 52 mg (8%) of 9-hydroxy-9-mesitylthioxanthene 10,10-dioxide (**34**) which was recrystallized from CH_2Cl_2–petroleum ether to form colorless prisms: mp 231–233 °C; IR (KBr) 3470 (OH), 1309 and 1146 cm^{-1} (SO_2); ^1H NMR ($CDCl_3$) δ 1.97 (br, $W_{1/2}$ = 0.24 ppm, 2- and 6-Me of mesityl group), 2.33 (s, 4-Me of mesityl group), 2.76 (br, OH), 6.88 (br s, H-3 and H-5 of mesityl group), 7.03–7.35 (m, H-1 and H-8), 7.37–7.73 (m Ar H), 8.04–8.35 (m, H-4 and H-5). Anal. Calcd for $C_{22}H_{20}O_3S$: C, 72.50; H, 5.53. Found: C, 72.64; H, 5.54.

9-Mesityl-9-(*p*-methoxyphenyl)thioxanthene (32). To an ethereal solution of *p*-methoxyphenylmagnesium bromide prepared from *p*-methoxyphenyl bromide (1.2 g), Mg (150 mg), ether (10 mL), and catalytic amounts of I_2 was added **36a** (1 g) in limited amounts under a nitrogen atmosphere. After addition of THF (20 mL), the mixture was refluxed for 5 h and hydrolyzed by adding an NH_4Cl solution. The reaction mixture was extracted with ether, washed with water, dried over anhydrous $MgSO_4$, and concentrated to dryness. The resulting oil was purified by preparative thin-layer chromatography on silica gel using CH_2Cl_2–petroleum ether (1:3) to give 445 mg (44%) of **32** which was recrystallized from CH_2Cl_2–petroleum ether to form colorless prisms: mp 211–213 °C.

Registry No. **4**, 36943-39-2; **5a**, 90133-31-6; **5b**, 90133-57-6; **6a**, 53512-25-7; **6b**, 66572-01-8; **7a**, 90133-33-8; **7b**, 90133-62-3; **7c**, 90133-64-5; **7d**, 66571-82-2; **7e**, 66571-84-4; **7f**, 66571-86-6; **9a**, 90133-34-9; **9b**, 90133-65-6; **9c**, 90133-66-7; **9d**, 66571-96-8; **9e**, 66571-97-9; **9f**, 66571-98-0; **10b**, 72751-72-5; **10c**, 72751-73-6; **10f**, 72731-25-0; **12**, 90133-55-4; **13**, 90133-58-7; **14**, 583-68-6; **15**, 42872-73-1; **16**, 90133-35-0; **17**, 90133-36-1; **18**, 84964-63-6; **18**-ol, 90133-39-4; **19**, 90133-38-3; **20**, 90133-56-5; **21**, 90133-59-8; **22**, 73083-79-1; **24**, 90133-40-7; **28**, 90133-60-1; **27**, 90133-42-9; **29**, 90133-43-0; **30**, 90133-47-4; **32**, 90133-54-3; **34**, 72780-38-2; **35a**, 90133-44-1; **35b**, 90133-45-2; **36a**, 90133-53-2; **36b**, 90133-49-6; **37a**, 90133-50-9; **37b**, 90133-51-0; **38**, 73083-77-9; 2-ClC_6H_4CHO, 89-98-5; C_6H_5SH, 108-98-5; C_6H_5OMe, 100-66-3; 4-$MeOC_6H_4Br$, 104-92-7; MeI, 74-88-4; EtI, 75-03-6; PrI, 107-08-4; 3-MeC_6H_4SH, 108-40-7; mesityl bromide, 576-83-0; thioxanthone, 492-22-8; duryl bromide, 1646-53-3; 2,3,4-trimethylphenyl bromide, 40101-33-5; 1,2,3-trimethylbenzene, 526-73-8.

Supplementary Material Available: Characteristics of compounds **5b**, **6b**, **7b–f**, **9b–f**, **10c,f**, **12**, **13**, **20**, **21**, **25**, and **26** not described in the Experimental Section (5 pages). Ordering information is given on any current masthead page.

Silver(I) Interactions with Ketones. Site of Complexation with Acetophenones and Effectiveness as a Lewis Acid Catalyst[1]

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Aromatic ketones present three possible sites for complexation of Ag^+: the oxygen lone pair, the π electrons of the carbonyl bond, and the π electrons of the aromatic ring. Upfield shifts of ^{13}C chemical shifts of meta and para carbons of acetophenone in the presence of silver nitrate showed that Ag^+ complexes with the aromatic ring moiety in water. This contrasts with previous results in methylene chloride in which the carbonyl group is not hydrogen bonded to solvent and acts as an n donor toward Ag^+. In the solid state, an X-ray structure determination of (*p*-methylacetophenone)$_2AgBF_4$ showed that Ag^+ was tetracoordinated to two carbonyl oxygens (2.36 Å) and to two aromatic rings of different ketone molecules (2.55- and 2.72-Å distances to meta and ortho carbons, respectively). Thus in the solid state, acetophenone acts *both* as an n and π donor. The Ag–O bond was shorter than most Ag–O bonds and appears to contribute more to the stabilization of the complex than Ag^+ interactions with the benzene rings. An sp^2 hybridization at oxygen was indicated by an AgOC angle of 137° and the fact that Ag^+ is only 6.2° above the plane of the carbonyl bond. Although Ag^+ catalyzed an aldol condensation of acetophenone in 1,2-dichloroethane at 70–80 °C, rates of hydrogen exchange for acetone in deuterated water at 44 °C showed no catalytic activity of $AgNO_3$ or $LiNO_3$.

Complexes of Ag^+ with π donors (alkenes and aromatics) and n donors (amines and ethers) are well-known.[2] However, very little has been reported about Ag^+ interactions with ketones, an important class of compounds that could act as n or π donors.

Previous work in our laboratory[3] showed that both aliphatic and aromatic ketones acted as n donors toward $AgBF_4$ in methylene chloride. This result was based on comparison of ^{13}C chemical shift changes with model complexes (Et_2O–Ag^+, cyclohexene–Ag^+, and toluene–Ag^+) and IR data. However, in one isolated report[4] a linear free-energy relationship of formation constants suggested that in water Ag^+ complexed with the benzene moiety of acetophenone.

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