Syntheses and Reactions of 9-Substituted 10-Phenylthioxanthenium Salts: Negative Evidence for Thia-anthracene Oligomerisation

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Various 9-aryl-10-phenylthioxanthenium salts have been prepared and their stereochemistry determined by ^{1}H n.m.r. spectroscopy. Reactions of the 10-phenylthioxanthenium salts or 10-phenyl-10-thia-anthracenes with aryl-lithiums have been studied in order to investigate whether or not 10-thia-anthracenes cause oligomerisation. The 10-phenylthioxanthenium salts reacted with aryl-lithiums to give 9-phenylthioxanthenes in good yields. However, 10-phenylthioxanthenium salt (**19**) when treated with phenyl-lithium at −15 to −20 °C gave 9-phenylthioxanthenol (**38**) (17%) together with 9-phenylthioxanthene (**13**) because of the lability of 10-phenyl-10-thia-anthracene to air. 10-Phenyl-9-(*p*-tolyl)-10-thia-anthracene (**50**) generated *in situ* from the sulphonium salt (**22**) and lithium di-isopropylamide failed to react with *p*-tolyl-lithium. An isolable ylide, 9-benzoyl-10-phenyl-10-thia-anthracene (**52**) was treated with *p*-tolyl-lithium at 0 °C to give 9-benzoylthioxanthene (**4**) (82%). In contrast, 9,9,10-triphenylthioxanthenium salt (**24**) on treatment with phenyl-lithium gave a ring-opened product (**40**), a ring-contracted product (**41**), diphenyl sulphide (**42**), and 9,9-diphenylthioxanthene (**12**). These results indicate that the 10-phenyl-10-thia-anthracenes or the σ-sulphuranes of thioxanthenes do not cause oligomerisation.

It had been reported that 10-thia-anthracenes were produced by the reaction of thioxanthylium salts with aryl-lithiums.[1] However, treatment of 9,10-disubstituted thioxanthenium salts with bases afforded unstable ylides, 9,10-disubstituted 10-thia-anthracenes, which rearranged intramolecularly to 9,9-disubstituted thioxanthenes in good yields.[2] This outcome raised doubts about the 'stable 10-thia-anthracenes having the ylene structure.'

In 1974 Mislow and his co-workers re-examined the thiabenzenes and concluded that thiabenzenes are unstable ylides and that the products obtained from the reactions of thiopyrylium salts with aryl-lithiums are trimeric to hexameric materials. On the basis of this work they proposed a mechanism for oligomerisation of the thiabenzenes.[3] Hortmann and his co-workers reported independently that thiabenzenes synthesized by proton abstraction from the dihydrothiopyranium salts showed ylidic character.[4]

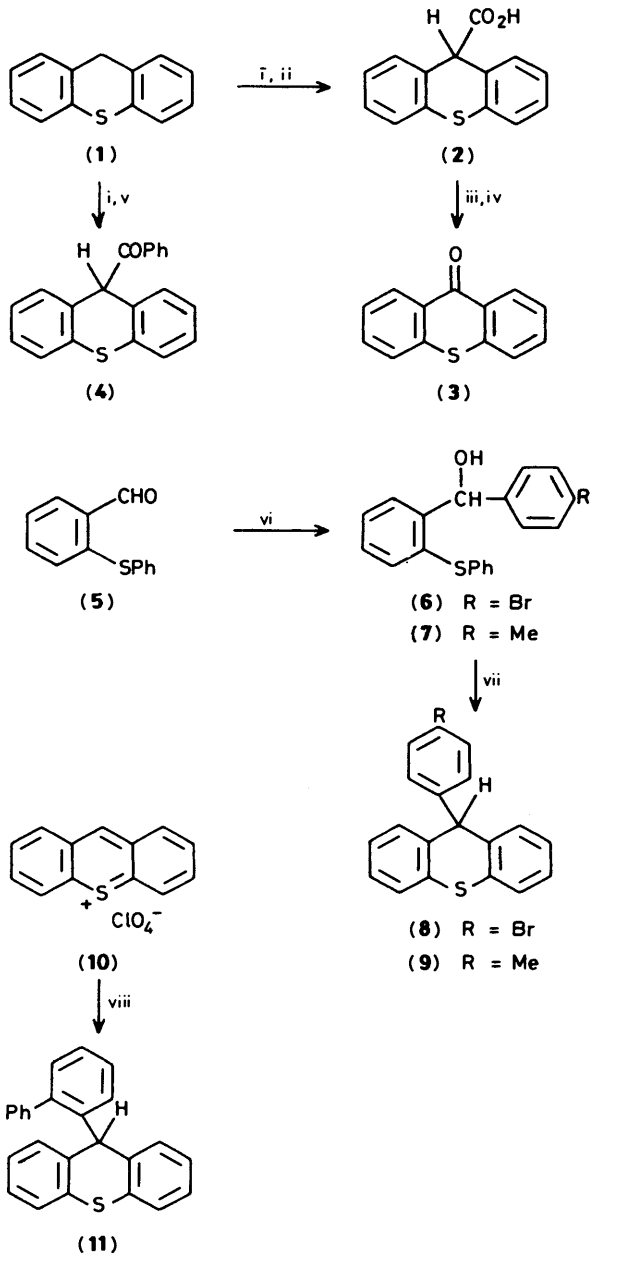
We re-examined the reaction of the 9-phenylthioxanthylium salt with phenyl-lithium and found that the products were mixtures of thioxanthenes formed by a radical reaction.[5] Price and Follweiler discussed the mechanistic pathways for oligomerisation of the 10-thia-anthracenes in which the pathway *via* a σ-sulphurane type intermediate is plausible and other pathways are excluded.[6] Therefore, the present report describes the syntheses of some 10-phenylthioxanthenium salts and their reactions with aryl-lithiums in order to elucidate the formation of the σ-sulphurane anions by a reaction of thiabenzene with organolithiums and oligomerisation of the σ-sulphurane anions. Stereochemistry of the 10-phenylthioxanthenium salts is also discussed on the basis of their ^{1}H n.m.r. spectral data.

Syntheses of 10-*Phenylthioxanthenium Salts.*—The synthesis of 9-benzoylthioxanthene (**4**) was attempted in two different ways: phenylation of thioxanthene-9-carboxylic acid (**2**)[7] and benzoylation of thioxanthene (**1**) (see Scheme 1). Neither phenylation of the acid (**2**) with 2 equiv. of phenyl-lithium nor chlorination followed by Friedel-Crafts phenylation gave compound (**4**), thioxanthone (**3**) being formed instead. The mechanism by which (**3**) is formed from (**2**) cannot, at present, be explained. An alternative route employing proton abstraction from (**1**) and successive benzoylation with 2-(benzoylthio)pyridine gave (**4**) (50%). 9-(*p*-Bromophenyl)- (**8**) and 9-(*p*-tolyl)-thioxanthene (**9**) were prepared in good yields by reactions of 2-(phenylthio)benzaldehyde (**5**) with *para*-substituted phenylmagnesium bromides followed by cyclisation with 80% sulphuric acid. 9-Biphenyl-2-ylthioxanthene (**11**) was synthesized by a reaction of the thioxanthylium salt (**10**) with biphenyl-2-ylmagnesium bromide. Other thioxanthenes were prepared by the reported methods (see Experimental section).

Phenylation of the thioxanthenes (**1**), (**4**), (**8**), (**9**), (**11**)—(**18**) with diphenyliodonium tetrafluoroborate[8] gave 10-phenylthioxanthenium tetrafluoroborates (**19**)—(**30**) in high yields. Exceptionally, 9-(*p*-methoxyphenyl)thioxanthene (**15**) afforded the *S*-phenyl sulphonium salt (**27**) (26.5%) together with a purple oil of undetermined structure. The sulphonium salts (**21**), (**22**), (**25**)—(**27**) consist of *cis*- and *trans*-isomers and two of them, (**25**) and (**26**), were separated by careful recrystallisation from acetic acid or chloroform: the *trans*-isomers (**25a**) and (**26a**) and the *cis*-isomers (**25b**) and (**26b**) were thus obtained. Physicochemical data of the sulphonium salts (**19**)—(**30**) were listed in Table 1.

Stereochemistry of 10-*Phenylthioxanthenium Salts.*—Thioxanthenium salts are pyramidally stable at sulphur and give rise to four possible conformational and configurational isomers (see Scheme 3). The results from an ^{1}H n.m.r. examination of these stereoisomers in trifluoroacetic acid are summarised in Table 2.

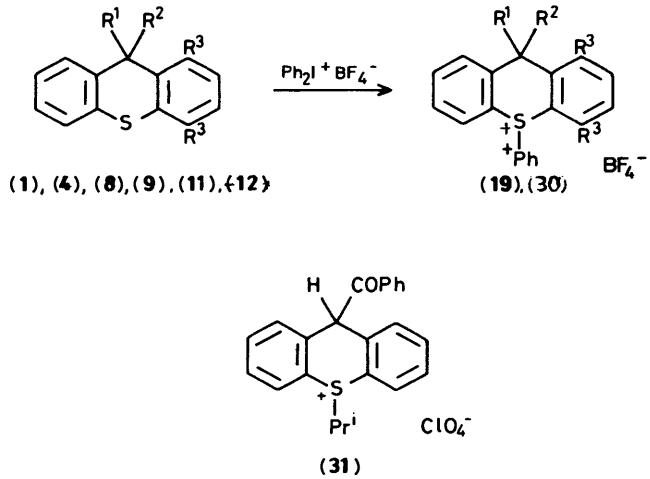
The stereochemical relationship between the 9- and 10-phenyl groups in the sulphonium salt (**25**) was ascertained by a comparison of the ^{1}H n.m.r. spectra with those of the 9-pentadeuteriophenyl derivative (**26**) and the 1,4-dimethyl-9,10-diphenyl congener (**30**). The ^{1}H n.m.r. spectrum of (**25b**) contains two multiplets at δ 6.38—6.75 and 6.78—7.1. These are absent in the spectrum of the pentadeuteriated derivative (**26b**) and are thus assigned to the signals of 2,6-H and 3,4,5-H of the 9-phenyl group in (**25b**). Thioxanthenium salts or sulphoxides with 1,4-peri-methyl groups take the pseudo-axial (*ax*) conformation at the 9- and 10-positions because of steric repulsion between the 9,10-substituents and the peri-methyl groups.[9,10] The 1,4-dimethyl-9,10-diphenylthioxanthenium salt (**30**) with 9*ax*,10*ax*-conformation exhibited upfield multiplets due to 9-phenyl protons in the same region (δ 6.35—6.7 and 6.7—7.05) as those referred to above in the spectrum of (**25b**), therefore the 9-phenyl group in (**25b**) is *ax*. Furthermore, the



Scheme 1. *Reagents:* i, BuLi; ii, CO_2; iii, PCl_5; iv, $AlCl_3$–PhH; v, PhCOS-2-Py; vi, *p*-RC_6H_4MgBr; vii, 80% (v/v) H_2SO_4; viii, *o*-PhC_6H_4MgBr

two multiplets in (**25b**) are upfield of those in the corresponding 10-alkyl-9-phenylthioxanthenium salts.[9] It is thus concluded that the 10-phenyl group in (**25b**) is also *ax*; were it pseudo-equatorial (*eq*) it would not affect the protons of the 9-phenyl group. The signals of the peri-protons (4,5-H) in (**25b**) and (**26b**) appear at lowfield (δ 8.15—8.35) due to the proximity of the positively charged sulphur atom. If the 10-phenyl group were *eq* these protons would be shielded by it and would resonate at higher fields than they do. They are not so shielded, therefore the 10-phenyl group is also *ax*. From these findings both phenyl groups in the *cis*-isomers (**25b**) and (**26b**) are *ax* (conformer A in Scheme 3).

On the other hand, two multiplets (δ 6.85—7.2 and 7.25—7.5) present in the ^1H n.m.r. spectrum of (**25a**) are absent in that of the corresponding deuteriated compound (**26a**), and can therefore be assigned to the 2,6-H and 3,4,5-H of the 9-phenyl

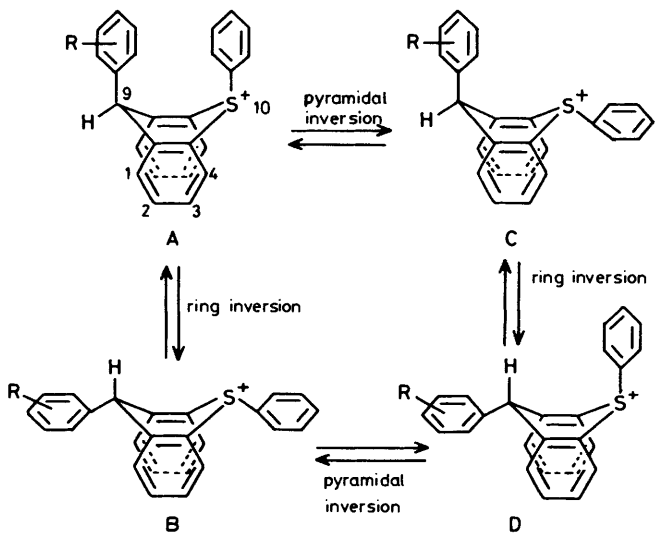


(**1**), (**4**), (**8**), (**9**), (**11**), (**12**) (**19**), (**30**)

(**31**)

(**1**), (**19**) $R^1 = R^2 = R^3 = H$
(**4**), (**20**) $R^1 = R^3 = H$, $R^2 = PhCO$
(**8**), (**21**) $R^1 = R^3 = H$, $R^2 = p\text{-}BrC_6H_4$
(**9**), (**22**) $R^1 = R^3 = H$, $R^2 = p\text{-}MeC_6H_4$
(**11**), (**23**) $R^1 = R^3 = H$, $R^2 = o\text{-}PhC_6H_4$
(**12**), (**24**) $R^1 = R^2 = Ph$, $R^3 = H$
(**13**), (**25**) $R^1 = R^3 = H$, $R^2 = Ph$
(**14**), (**26**) $R^1 = R^3 = H$, $R^2 = C_6D_5$
(**15**), (**27**) $R^1 = R^3 = H$, $R^2 = p\text{-}MeOC_6H_4$
(**16**), (**28**) $R^1 = R^3 = H$, $R^2 = 2,4,6\text{-}Me_3C_6H_2$
(**17**), (**29**) $R^1 = R^3 = H$, $R^2 = 2,3,5,6\text{-}Me_4CH$
(**18**), (**30**) $R^1 = H$; $R^2 = Ph$, $R^3 = Me$

Scheme 2.



Scheme 3.

group in the former. These signals are observed in the similar region to those in the ^1H n.m.r. spectra of 10-alkyl-9*ax*-phenylthioxanthenium salts.[9] The peri-protons (4,5-H) in (**25a**) appear at higher field than those in (**25b**), and it may thus be concluded that the 10-phenyl group in (**25a**) is *eq*. From these data the preferred conformation of the *trans*-isomers (**25a**) and (**26a**) is 9*ax*,10*eq* (conformer C in Scheme 3).

The foregoing conclusions about the *cis*- and *trans*-isomers of (**25**) and (**26**) are supported by the ^1H n.m.r. signal of the proton at C-9. In (**30**) both 9- and 10-phenyl groups are definitely *ax* and the 9*eq*-H appears at δ 6.05. In both the *cis*- and *trans*-

Table 1. 10-Phenylthioxanthenium salts (**19**)—(**30**)

Compd.	Yield (%)	Appearance* (Recryst. solv.)	M.p. (°C)	Formula	Analysis (%) Required (Found) C	H
(**19**)	85	CN (Me_2CO–Et_2O)	171—172	$C_{19}H_{15}BF_4S$	63.0 (62.8)	4.2 (4.1)
(**20**)	95.5	CN (AcOH–Et_2O)	211—212	$C_{26}H_{19}BF_4OS$	67.0 (67.0)	4.1 (4.1)
(**21**)	76.5	CP (Me_2CO–Et_2O)	210—214	$C_{25}H_{18}BBrF_4S$	58.1 (57.8)	3.5 (3.45)
(**22**)	93	CP (Me_2CO–Et_2O)	220—222	$C_{26}H_{21}BF_4S$	69.0 (69.1)	4.7 (4.7)
(**23**)	80	CP (Me_2CO–Et_2O)	227—230	$C_{31}H_{23}BF_4OS$	72.4 (72.4)	4.5 (4.6)
(**24**)	56	CP (AcOH–Et_2O)	291—292	$C_{31}H_{23}BF_4S$	72.4 (72.5)	4.6 (4.6)
(**25a**)	78	CN (AcOH)	262—264[a]	$C_{25}H_{19}BF_4S$	68.5 (68.5)	4.4 (4.4)
(**25b**)		CP ($CHCl_3$)	263—265[a]	$C_{25}H_{19}BF_4S$·1/3$CHCl_3$	62.8 (62.7)	4.1 (4.0)
(**26a**)	61	CN (AcOH)	261—262[a]	$C_{25}H_{14}BD_5F_4S$	[c]	
(**26b**)		CP ($CHCl_3$)	263—264[a]	$C_{25}H_{14}BD_5F_4S$	[c]	
(**27**)	26.5	CP (Me_2CO–Et_2O)	186—188	$C_{26}H_{21}BF_4OS$	66.7 (66.6)	4.5 (4.3)
(**28**)	83	CP (AcOH–Et_2O)	224—225[b]	$C_{28}H_{25}BF_4S$	70.0 (70.1)	5.25 (5.4)
(**29**)	71	CP ($CHCl_3$–Et_2O)	235—238[b]	$C_{29}H_{27}BF_4S$	70.45 (70.2)	5.5 (5.5)
(**30**)	82	CP (Me_2CO–Et_2O)	256—259	$C_{27}H_{23}BF_4S$	69.5 (69.3)	5.0 (4.9)

* CP = Colourless prisms, CN = colourless needles.

[a] The isomer changed into the other during the measurement and therefore both isomers showed similar m.p.s. [b] With decomposition. [c] Elemental analyses of the deuteriated compounds (**26a**—**b**) were not performed using a Yanagimoto CHN recorder MT-3 analyser.

Table 2. ^{1}H N.m.r. spectral data of 10-phenylthioxanthenium salts (**19**)—(**30**) in CF_3CO_2H (δ)

Compd.	9-H	ArH	Methyl protons	Isomer ratio
(**19**)	3.96[a] 4.45[a]	7.15—7.5 (2 H, m, 2,6-H or 10-Ph), 7.5—8.0 (9 H, m, ArH), 8.0—8.35 (2 H, m, 4,5-H)		
(**20**)	6.95	7.2—7.5 (2 H, 2,6-H of 10-Ph), 7.5—7.75 (3 H, 3,4,5-H of 10-Ph), 7.75—7.95 (9 H, m, ArH), 7.95—8.1 (2 H, m, 4,5-H), 8.34 (2 H, dd, *J* 7.5, 1.5 Hz, 2,6-H of 9-COPh)		D
(**21**)	5.48 5.75	6.35 (d, *J* 8 Hz, 2,6-H of 9a′-Ar), 6.75—7.35 (m, 3,5-H of 9a′-Ar and 10a′-Ph), 7.4—8.1 (m, ArH), 8.1—8.35 (m, 4,5-H)		A/C = 0.8
(**22**)	5.48 5.80	6.4 (d, *J* 8 Hz, 2,6-H of 9a′-Ar), 6.7 (d, *J* 8 Hz, 3,5-H of 9a′-Ar), 6.75—7.1 (m, 2,6-H of 10a′-Ph), 7.5—8.15 (m. ArH), 8.15—8.35 (m, 4,5-H)	2.15, 2.4 (s, Me of 9a′-Ar)	A/C = 0.8
(**23**)	5.18	6.8—8.0 (18 H, m, ArH), 8.1—8.4 (2 H, m, 4,5-H)		D
(**24**)		6.58—6.9 (2 H, m, 2,6-H of 9-Ph), 6.95—7.9 (19 H, m, ArH), 7.95—8.2 (2 H, m, 4,5-H)		
(**25a**)	5.50	6.85—7.2 (2 H, m, 2,6-H of 10-Ph), 7.25—7.5 (3 H, m, 3,4,5-H of 10-Ph), 7.5—8.0 (13 H, m, ArH)		C
(**25b**)	5.83	6.38—6.75 (2 H, m, 2,6-H of 9-Ph), 6.78—7.1 (6 H, m, 3,4,5-H of 9,10-Ph), 7.05—7.43 (2 H, m, 2,6-H of 10-Ph), 7.7—8.13 (6 H, m, ArH), 8.15—8.35 (2 H, m, 4,5-H)		A
(**26a**)	5.50	7.4—8.0 (13 H, m, ArH)		C
(**26b**)	5.83	6.75—7.1 (3 H, 3,4,5-H of 10-Ph), 7.05—7.43 (2 H, m, 2,6-H of 10-Ph), 7.67—8.1 (6 H, m, ArH), 8.15—8.35 (2 H, m, 4,5-H)		A
(**27**)	5.50 5.80	6.53 (s, 2,3,5,6-H of 9a′-Ar), 6.78—7.1 (m, 3,4,5-H of 10a′-Ph), 7.05—7.45 (m, 2,6-H of 10a′-Ph), 7.35—8.1 (m, ArH), 8.2—8.35 (m, 4,5-H)	3.85, 4.00 (s, OMe of 9a′-Ar)	A/C = 0.7
(**28**)	5.53	7.0—8.05 (13 H, m, ArH), 8.15—8.5 (2 H, m, 4,5-H)	1.25—1.75, 1.75—2.3 (6 H, br s, 2,6-Me of 9-Ar), 2.40 (3 H, s, 4-Me of 9-Ar)	D
(**29**)	5.63	7.1—8.0 (12 H, m, ArH), 8.15—8.5 (2 H, m, 4,5-H)	1.38, 1.98 (6 H, s, 2,6-Me of 9-Ar), 2.28, 2.40 (6 H, s, 3,5-Me of 9-Ar)	D
(**30**)	6.05	6.35—6.7 (2 H, m, 2,6-H or 9-Ph), 6.7—7.05 (6 H, m, 3,4,5-H of 9,10-Ph), 7.05—7.4 (2 H, m, 2,6-H of 10-Ph), 7.4—8.2 (5 H, m, ArH), 8.2—8.45 (1 H, m, 5-H)	2.65 (3 H, s, 1-Me), 2.91 (3 H, s, 4-Me)	A

[a] Doublets with *J* 19.0 Hz.

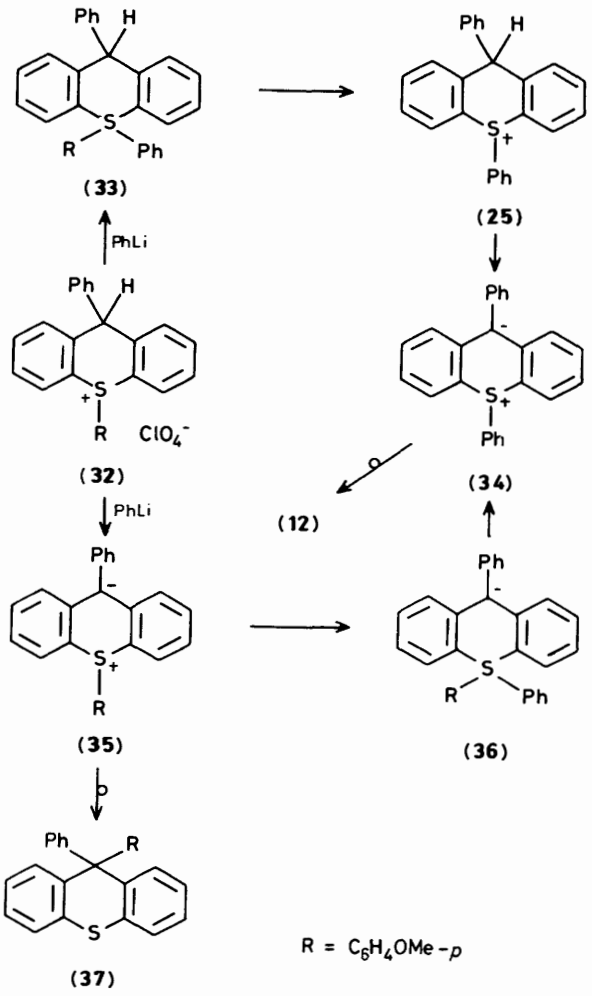
isomers of (**25**) and (**26**) the 9-phenyl group is *ax* and the 9-H is *eq*. However, the signal of 9*eq*-H (δ 5.50) of 10*eq*-phenylthioxanthenium salt (**25a**) appears higher than that (δ 5.83) of 10*ax*-phenyl isomer (**25b**). Although individual stereoisomers were not separated for salts (**21**), (**22**), and (**27**), their ^{1}H n.m.r. spectra indicated that both *cis*- and *trans*- forms were present.

We now turn to 9-mesityl- (**28**) and 9-(2,3,5,6-tetramethylphenyl)-10-alkylthioxanthenium salt (**29**). The 9-aryl group which carries several methyl groups is *eq* in the 10-alkyl counterparts,[9] 10-oxides and 10,10-dioxides.[11] On the evidence of the signals of the methyl groups in the 9-aryl substituent, the same is true for (**28**) and (**29**). The resonances of the peri-protons (4,5-H) are consistent with the 10*ax*-conformation. Similar considerations to all those above show that the 9-benzoyl- (**20**) and 9-biphenyl-2-yl-10-phenyl- (**23**) salts exist in the 9*eq*,10*ax*-conformations (conformer D in Scheme 3).

The 10-phenylthioxanthenium salts having 9*ax*,10*ax*-conformation (conformer A) are good tools for the studies of the through-space interaction.[12]

Reaction of 10-*Phenylthioxanthenium Salts with Aryllithiums.*—10-Substituted 10-thia-anthracenes generated by deprotonation of thioxanthenium salts with bases are stable at low temperature and rearrange easily to 9-substituted thioxanthenes.[2,3] From this evidence, it is doubtful whether the thia-anthracenes decompose to the oligomeric materials.[3] However, Price and Follweiler believed Mislow's hypothesis for the formation of oligomeric materials and applied it as an explanation of their reactions.[6] We studied the reactions of some 10-thia-anthracenes with aryl-lithiums in order to clarify any doubt. First of all we discuss the reaction of 10-(*p*-methoxyphenyl)-9-phenylthioxanthenium salt (**32**) with phenyllithium giving 9-(*p*-methoxyphenyl)-9-phenylthioxanthene (**37**) and a ligand-exchanged product, 9,9-diphenylthioxanthene (**12**).[2b] An intermediate, 9,10-diphenyl-10-thia-anthracene (**34**) is probably formed by way of substitution on the positive sulphur atom and then abstraction of 9-H as shown in Scheme 4. If the thia-anthracene were generated through the reverse process, abstraction and then replacement, the first intermediate, 10-(*p*-methoxyphenyl)-9-phenyl-10-thia-anthracene (**35**) reacts with phenyl-lithium to produce the σ-sulphurane anion intermediate (**36**) and changes into 9,10-diphenyl-10-thia-anthracene (**34**), which affords 9,9-diphenylthioxanthene (**12**) finally. This assumption is against Mislow's postulation of oligomerisation of the sulphurane anion. Therefore, we examined the reaction of 10-phenylthioxanthenium salts with aryl-lithiums at low temperature, where rearrangement of the 10-thia-anthracenes is retarded and an excess of aryl-lithium may attack the 10-thia-anthracenes to form the σ-sulphurane anions.

A mixture of *cis*- and *trans*-isomers of 9,10-diphenylthioxanthenium salt (**25**) was treated with phenyl-lithium with ice-cooling or at −60 °C for 3 h and then at room temperature overnight to give 9,9-diphenylthioxanthene (**12**) in 72.5 or 81% yield, respectively. Reaction of 10-phenylthioxanthenium salt (**19**) with phenyl-lithium at −15 to −20 °C afforded 9-phenylthioxanthene (**13**) (57%) and 9-phenylthioxanthenol (**38**) (17%). Other products exhibiting *m*/*z* 546 and 578 in their e.i. mass spectra were obtained, but their amounts were too small to determine their structures. Although Price and Follweiler had obtained the thioxanthene (**13**) from the reaction of the thioxanthenium salt (**19**) with phenyl-lithium at −12 and 25 °C in 42 and 80—90% yields, respectively; they did not isolate the thioxanthenol (**38**). They described that the thioxanthene (**13**) decreased at −12 °C because of formation of the oligomeric products and discussed the plausible mechanisms for oligomer formation. However, since the oligomeric products were not obtained from the reaction of (**25**) with phenyl-lithium,

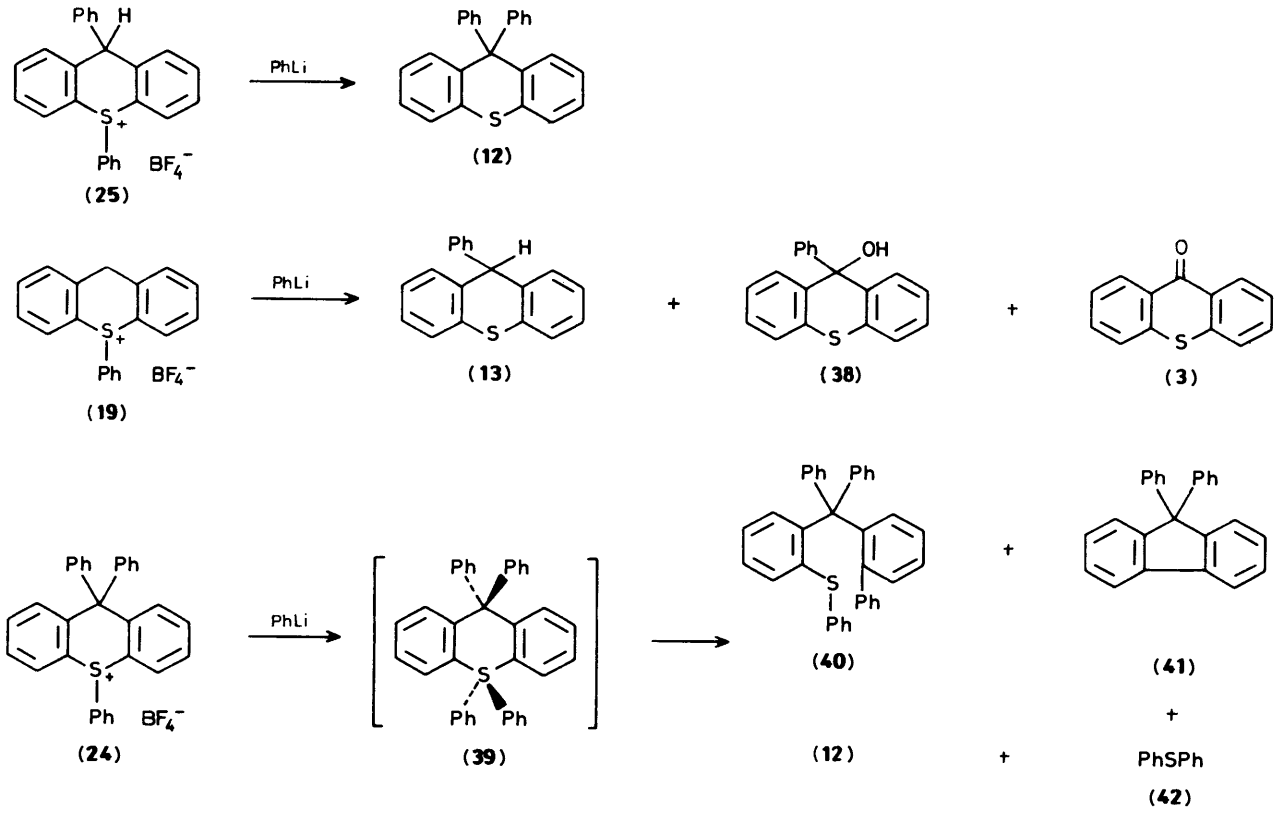


Scheme 4.

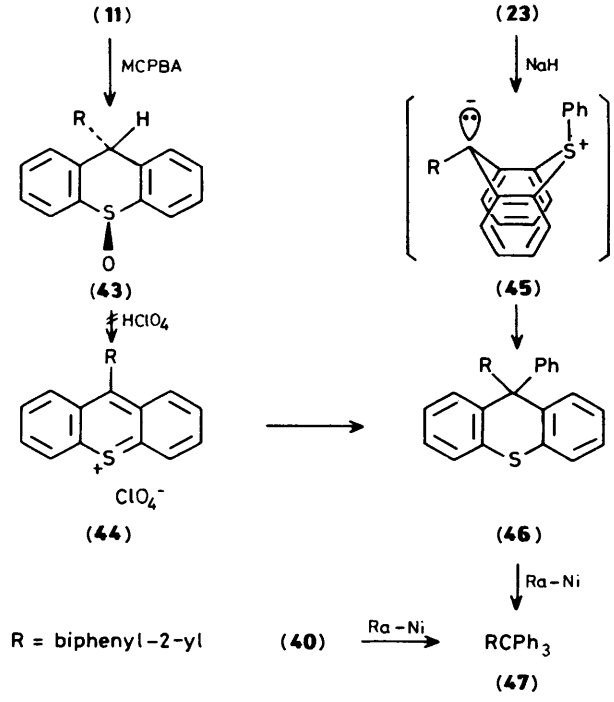
we assumed that the lack of a substituent at 9-position complicated the reaction of the thioxanthenium salt (**19**) with phenyl-lithium. Therefore, the reaction of the 9,9-disubstituted sulphonium salt (**24**) with phenyl-lithium was next examined (Scheme 5).

Reaction of the 9,9,10-triphenylthioxanthenium salt (**24**) having no 9-H with phenyl-lithium gave a ring-opened product, biphenyl-2-yl(diphenyl)(*o*-phenylthiophenyl)methane (**40**) (56%), 9,9-diphenylfluorene (**41**) (20.5%), diphenyl sulphide (**42**) (17%), and 9,9-diphenylthioxanthene (**12**) (9%). The reaction mechanism can be explained as occurring *via* the σ-sulphurane (**39**). This result is similar to that of the reaction of 9,9-dimethyl-10-phenylthioxanthenium salt with phenyl-lithium, although the latter reaction failed to afford the ring-contracted product, 9.9-dimethylfluorene or its counterpart (**42**).[13] Steric repulsion between the 9-phenyl group and 1,8-H would advantageously serve the coupling of two carbons bound to the sulphur atom of the thioxanthene ring in the σ-sulphurane intermediate (**39**). From this experiment the σ-sulphurane (**39**) did not form the oligomeric materials.

The reaction products (**12**) and (**40**)—(**42**) were identified with authentic samples. The structure of the ring-opened product (**40**) was determined by identification of the desulphurised product (**47**) with an unambiguous sample as shown in Scheme 6. Biphenyl-2-yl(triphenyl)methane (**47**) can be derived by desulphurisation of 9-biphenyl-2-yl-9-phenylthioxanthene (**46**), the latter formed by treating the 9-biphenyl-2-ylthioxanthylium salt (**44**) with phenylmagnesium bromide.



Scheme 5.



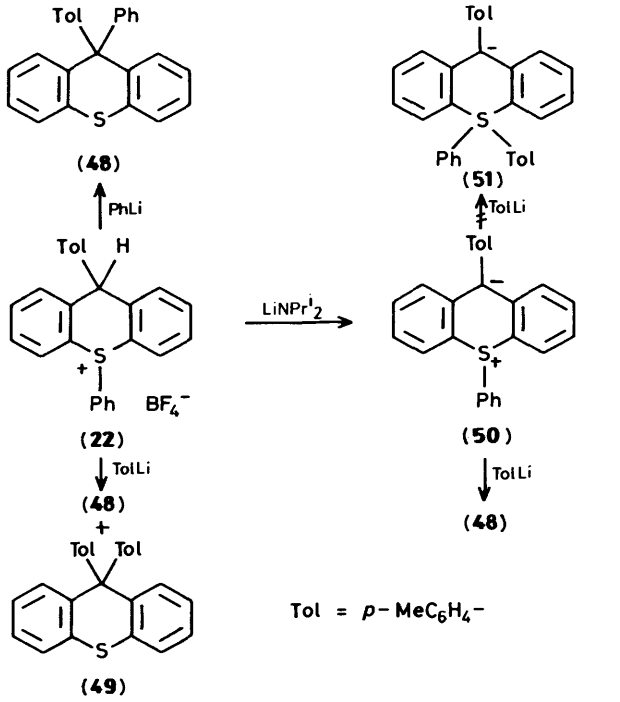
Scheme 6.

However, treatment of *trans*-9-biphenyl-2-ylthioxanthene 10-oxide (**43**) with 70% perchloric acid failed to give the thioxanthylium salt (**44**), probably because steric interaction between the 9-biphenyl-2-yl group and the thioxanthene ring makes it difficult for 9-C to achieve an sp^2 planar configuration. In view of this we treated the 10-phenylthioxanthenium salt (**23**) with sodium hydride in order to generate a thia-anthracene (**45**) which possesses an sp^3 carbanion at 9-C. The latter then easily rearranged to a thioxanthene (**46**) (88%) because of its 9*ax*-carbanion and 10*ax*-phenyl conformation. Desulphurisation of (**46**) with Raney-Ni afforded biphenyl-2-yl(triphenyl)methane (**47**) (42%).

From these observations of the reactions of compounds (**24**) and (**25**), a decrease of compound (**13**) in the reaction of compound (**29**) with phenyl-lithium at low temperature is attributed to complex side-reactions not at the sulphur atom but at 9-C. Rearrangement of 10-phenyl-10-thia-anthracene is decelerated at low temperature, the thia-anthracene reacting with any air present as a contaminant under a nitrogen atmosphere to form the thioxanthone (**3**); the latter affords compound (**38**) by reaction with phenyl-lithium. Although we cannot provide a detailed explanation for the above reaction, that the side-products (**3**) and (**38**) increased significantly when (**19**) was treated with phenyl-lithium in the presence of air supports the mode of formation suggested.

The reactions of 9-(*p*-tolyl)-10-phenylthioxanthenium salt (**22**) with aryl-lithiums gave similar results to the reactions of (**32**) with aryl-lithiums.

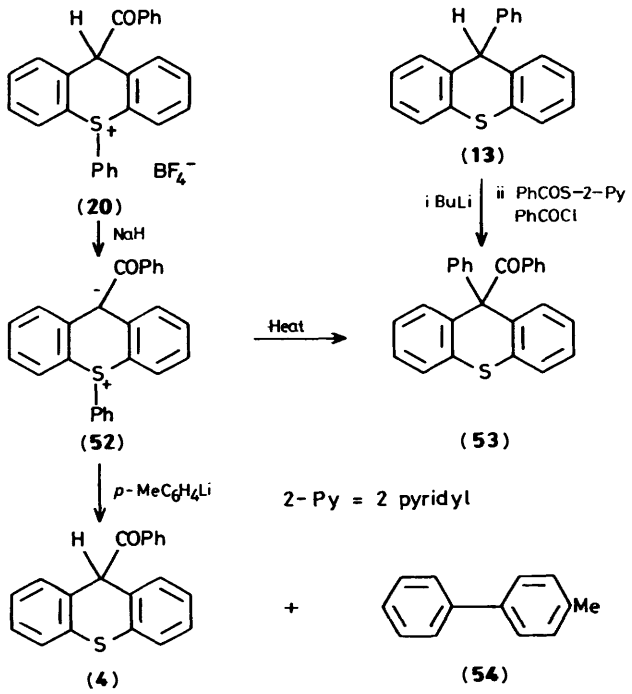
Treatment of the thioxanthenium salt (**22**) with phenyl-lithium gave 9-phenyl-9-(*p*-tolyl)thioxanthene (**48**) (89%) and with *p*-tolyl-lithium a mixture of compound (**48**) and 9,9-di(*p*-tolyl)thioxanthene (**49**) in a ratio of 2.4:1. Formation of compound (**49**) can be explained in terms of a ligand-exchange mechanism similar to that for the reaction of compound (**32**) and phenyl-lithium shown (see Scheme 4). We also examined the reaction of 10-phenyl-9-(*p*-tolyl)-10-thia-anthracene (**50**) with *p*-tolyl-lithium in order to investigate the formation of a σ-sulphurane anion, the latter being an important intermediate for thiabenzene oligomerisation in Mislow's hypothesis. The



Scheme 7.

thia-anthracene (**50**), generated by reaction of compound (**22**) with lithium di-isopropylamide at −60 °C, was allowed to react with *p*-tolyl-lithium to afford compound (**48**) (68%). This suggests that rearrangement of the thia-anthracene (**50**) into the thioxanthene (**48**) is much faster than nucleophilic attack of *p*-tolyl-lithium on (**50**) and formation of the σ-sulphurane anion (**51**).

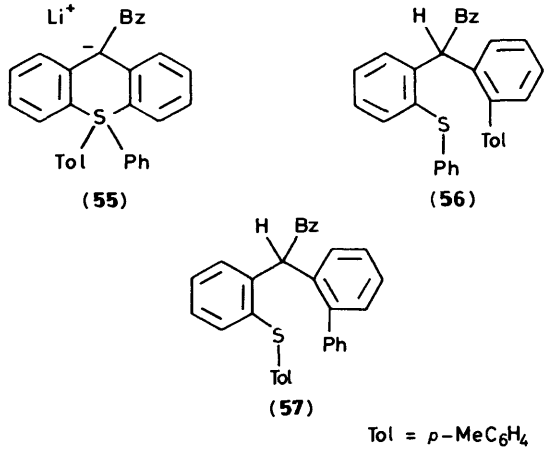
Finally, we synthesized an isolable 10-thia-anthracene and treated it with an organolithium (Scheme 8). Thus, the sulphonium salt (**20**) on treatment with sodium hydride in acetonitrile gave 9-benzoyl-10-phenyl-10-thia-anthracene (**52**) (79%). The assignment of its ylidic structure is supported by the absence of an n.m.r. signal for 9-H (δ_H *ca.* 5.9) and the presence of broad, strong absorption for the ylide carbonyl group at 1 540—1 480 cm^{-1} [shifted by 135—200 cm^{-1} to the lower frequency compared with that for the carbonyl group of (**20**)].



Scheme 8.

The ylide (**52**) underwent the thermal rearrangement in refluxing in benzene to afford 9-benzoyl-9-phenylthioxanthene (**53**) in quantitative yield. The structure of (**53**) was confirmed by comparison with an authentic specimen prepared (62%) by deprotonation and benzoylation of (**13**).

The ylide (**52**) was allowed to react with *p*-tolyl-lithium (2 equiv.) at 0 °C in the expectation that a σ-sulphurane anion would result and that this would give rise to oligomers. The dephenylated product (**4**) was obtained in 82% yield and the accompanying product 4-methylbiphenyl (**54**) was identified by comparison with an authentic sample (h.p.l.c.). This finding rules out a path whereby *p*-tolyl-lithium attacks the positive sulphur of (**52**) to form the σ-sulphurane anion (**55**), which then collapses to oligomers. It is possible that the intermediate (**55**) produces compounds (**4**) and (**54**). However, our earlier studies on σ-sulphuranes of thioxanthenes[13] and the reaction of compound (**24**) described above indicates that the σ-sulphuranes



afford ring-opened products. Therefore, if (**55**) were an intermediate for (**4**) and (**54**), the ring-opened products, (**56**) and (**57**) should be formed. Since, however these compounds were not detected, the preferable pathway for the formation of compounds (**4**) and (**54**) would be the attack of *p*-tolyl-lithium at an ipso carbon of the *S*-phenyl group.

We conclude that the reaction of 10-thia-anthracenes with aryl-lithium does not produce the oligomeric materials.

Experimental

M.p.s were determined on a Yanagimoto micro-melting point apparatus and are uncorrected. I.r. spectra were recorded on a JASCO A-1 spectrometer. ^{1}H N.m.r. spectra were measured on a Hitachi R-20B spectrometer with tetramethylsilane as an internal standard. The values are expressed in parts per million (δ). E.i. mass spectra were obtained on a JEOL D-300 spectrometer.

Materials.—The following thioxanthenes were prepared by the known methods: thioxanthene (**1**),[14] 9,9-diphenylthioxanthene (**12**),[1a] 9-phenylthioxanthene (**13**),[1a] 9-pentadeuteriophenylthioxanthene (**14**),[11] 9-(*p*-methoxyphenyl)-thioxanthene (**15**),[1b] 9-mesitylthioxanthene (**16**),[15] 9-(2,3,5,6-tetramethylphenyl)thioxanthene (**17**),[15] and 1,4-dimethyl-9-phenylthioxanthene (**18**).[11]

9-*Benzoylthioxanthene* (**4**).—A solution of (**1**) (3 g) in dry THF (50 ml) was gradually added to a stirred ethereal solution of butyl-lithium (30 ml) at 0 °C under nitrogen. The reaction mixture was warmed to room temperature and then stirred for 2 h. The resulting dark red solution was cooled to 0 °C when 2-benzoylthiopyridine[16] (4.8 g) in dry benzene (40 ml) was added to it. The reaction mixture was stirred for 30 min at 0 °C and then quenched with water. The organic layer was separated and the aqueous layer was extracted with benzene. The organic layer and the extract were combined, dried ($MgSO_4$), and evaporated. The residue was chromatographed on silica gel using hexane and hexane–benzene (1:1) as eluant to give the starting material (**1**) from the hexane fraction and the product (**4**) from the hexane–benzene (1:1) fraction. Recrystallisation of (**4**) from chloroform–hexane gave yellow needles (2.3 g, 50%), m.p. 129—130 °C; $\nu_{max.}$ 1 680 cm^{-1} (CO); δ 5.86 (1 H, s, 9-H), 7.0—7.55 (11 H, m, ArH), and 7.84—8.05 (2 H, m, 2,6-H of PhCO) (Found: C, 79.5; H, 4.7. $C_{20}H_{14}OS$ requires C, 79.4; H, 4.7%).

p-*Bromophenyl*[o-(*phenylthio*)*phenyl*]*methanol* (**6**).—A solution of *o*-(phenylthio)benzaldehyde (**5**)[16] (4.0 g) in dry ether (20 ml) was added to a solution of *p*-bromophenylmagnesium bromide [prepared from *p*-dibromobenzene (7.1 g) and magnesium (0.7 g)] in dry ether (50 ml). The reaction mixture was refluxed for 3 h, cooled, and decomposed with water. The organic layer was separated and the aqueous layer was extracted with benzene. The combined extracts were dried ($MgSO_4$) and evaporated. The residue was column chromatographed on silica gel using dichloromethane–hexane (1:3) as eluant and recrystallised from dichloromethane–hexane to give colourless plates (6.1 g, 88%), m.p. 67 °C; $\nu_{max.}$ 3 300 cm^{-1} (OH); δ 2.71 (1 H, d, *J* 4.0 Hz, OH), 6.28 (1 H, d, *J* 4.0 Hz, CH), and 7.0—7.7 (13 H, m, ArH) (Found: C, 61.7; H, 4.1. $C_{19}H_{15}BrOS$ requires C, 61.5; H, 4.1%).

p-*Tolyl*[o-(*phenylthio*)*phenyl*]*methanol* (**7**).—A solution of the aldehyde (**5**) (8.6 g) in dry ether (50 ml) was added to a solution of *p*-tolylmagnesium bromide [prepared from *p*-bromotoluene (10.3 g) and magnesium (1.5 g)] in dry ether (100 ml). The mixture was refluxed for 7 h and worked up as above. Recrystallisation from dichloromethane–hexane gave colourless needles (11.2 g, 91%), m.p. 90 °C; $\nu_{max.}$ 3 420 cm^{-1} (OH); δ 2.29 (3 H, s, Me), 2.48 (1 H, br s, OH), 6.30 (1 H, s, CH), and 7.0—7.75 (13 H, m, ArH) (Found: C, 78.5; H, 5.9. $C_{20}H_{18}OS$ requires C, 78.4; H, 5.9%).

9-(p-*Bromophenyl*)*thioxanthene* (**8**).—A mixture of the alcohol (**6**) (5 g) and 80% (v/v) sulphuric acid (25 ml) was heated on a water-bath for 45 min with occasional shaking. The cooled reaction mixture was poured onto ice and extracted with dichloromethane. The extract was dried and evaporated. The oily product was solidified and recrystallised from dichloromethane–hexane to give colourless needles (4.0 g, 84%), m.p. 126—127 °C; δ 5.28 (1 H, s, 9-H), 6.85 (2 H, d, *J* 8.2 Hz, 2,6-H of 9-Ar), and 7.05—7.65 (10 H, m, ArH) (Found: C, 64.6; H, 3.7. $C_{19}H_{13}BrS$ requires C, 64.6; H, 3.7%).

9-(p-*Tolyl*)*thioxanthene* (**9**).—A mixture of the alcohol (**7**) (7 g) and 80% (v/v) sulphuric acid (50 ml) was heated on a water-bath for 1 h with occasional shaking. The mixture was worked up as above. Recrystallisation from ethanol gave colourless needles (6.2 g, 94%), m.p. 148—149 °C; δ 8.20 (3 H, s, Me), 5.25 (1 H, s, 9-H), 6.93 (4 H, s, 9-ArH), and 7.05—7.6 (8 H, m, ArH) (Found: C, 83.4; H, 5.65. $C_{20}H_{16}S$ requires C, 83.3; H, 6.0%).

9-*Biphenyl*-2-*ylthioxanthene* (**11**).—Thioxanthylium perchlorate (**10**)[1a] (10 g) was added to a solution of biphenyl-2-ylmagnesium bromide [prepared from 2-bromobiphenyl (15.7 g) and magnesium (1.6 g)] in dry ether (50 ml). The reaction mixture was refluxed for 15 h, cooled, and decomposed with water. The organic layer was separated and the aqueous layer was extracted with ether. The combined extracts were dried ($MgSO_4$) and evaporated. The residue was column chromatographed on silica gel using dichloromethane–hexane (1:10) as eluant and recrystallised from dichloromethane–hexane to give colourless needles (3.8 g, 32%), m.p. 158—159 °C; δ 5.35 (1 H, s, 9-H) and 6.75—7.5 (17 H, m, ArH) (Found: C, 85.6; H, 5.3. $C_{25}H_{18}S$ requires C, 85.7; H, 5.2%).

General Procedure for 10-*Phenylthioxanthenium Tetrafluoroborates* (**19**)—(**30**).—The method of Crivello and Lam[8] was modified for the preparation of 10-phenylthioxanthenium salts. Equimolar proportions of thioxanthene and diphenyliodonium tetrafluoroborate[17] in the presence of cupric benzoate (0.24 mol equiv.) in *s*-tetrachloroethane (5 ml per 2 g of thioxanthenes) were stirred and heated at 125—135 °C under nitrogen for 3—5 h. The cooled reaction mixture was added dropwise into ether or THF with stirring. The precipitate was filtered off and recrystallised from an appropriate solvent. Yields, m.p.s, and analytical data are summarised in Table 1 and ^1H n.m.r. spectral data are shown in Table 2.

9-*Benzoyl*-10-*isopropylthioxanthenium Perchlorate* (**31**).—Silver perchlorate (686 mg) was added to a solution of compound (**4**) (1 g) and isopropyl iodide (5.6 g) in 1,2-dichloroethane (15 ml) and the mixture was stirred for a week. The precipitate was filtered off and washed with hot acetonitrile. The washings were concentrated to give a residual solid. Recrystallisation from acetonitrile–ether afforded colourless prisms (140 mg, 9.5%), m.p. 130—131 °C (decomp.); $\nu_{max.}$ 1 780 (CO) and 1 100 cm^{-1} (ClO_4^-); δ 1.83 (6 H, d, *J* 6.8 Hz, Me), 4.65 (1 H, sept., *J* 6.8 Hz, CH), 6.88 (1 H, s, 9-H), 7.40—8.15 (11 H, m, ArH), and 8.30 (2 H, dd, *J* 6.8, 2.0 Hz, 3,6-H or 9-COPh) (Found: C, 62.2; H, 4.8. $C_{23}H_{21}ClO_5S$ requires C, 62.1; H, 4.8%).

Reaction of 9,10-*Diphenylthioxanthenium Tetrafluoroborate* (**25**) *with Phenyl-lithium*.—Phenyl-lithium (0.96M; 11 ml) was added to a stirred suspension of compound (**25**) (500 mg) in dry THF (10 ml) at −60 °C under nitrogen. The mixture was stirred for 3 h at that temperature and then gradually warmed to room temperature. After being stirred overnight, the mixture was decomposed with water and extracted with benzene. The extracts were dried ($MgSO_4$) and concentrated under reduced pressure. The residual solid was chromatographed on silica gel using benzene–hexane (1:10) as eluant to give 9,9-diphenylthioxanthene (**12**) (325 mg, 81%). When the reaction was conducted at 0 °C, the thioxanthene (**12**) was obtained (72.5%).

Reaction of 10-*Phenylthioxanthenium Tetrafluoroborate* (**19**) *with Phenyl-lithium*.—(*a*) Phenyl-lithium (1.1M; 5.5 ml) was added to a stirred suspension of the sulphonium salt (**19**) (500 mg, 1.4 mmol) in dry ether (30 ml) at −15 to −20 °C under nitrogen. The reaction mixture was stirred for 24 h at that temperature and then decomposed with water. The organic layer was separated and the aqueous layer was extracted with ether. The extracts were dried ($MgSO_4$) and evaporated under reduced pressure. The residue was chromatographed on silica gel using benzene–hexane (1:10) as eluant to give 9-phenylthioxanthene (**13**) (0.21 g, 57%) and 9-phenylthioxanthenol (**38**) (69 mg, 17%).

(*b*) The reaction was carried out on the same scale as method (*a*). The reaction mixture was stirred at −20 °C for 15 min after addition of phenyl-lithium and air was slowly passed over the reaction mixture for 2 h. The mixture was decomposed with water and extracted with benzene. The extracts were dried ($MgSO_4$) and evaporated under reduced pressure. The residue

was chromatographed on silica gel using benzene–hexane (1:10 and 2:5) as eluant to give (**13**) (65 mg, 17%), (**38**) (79 mg, 20%), and thioxanthone (**3**) (56 mg, 19%).

Reaction of 9,9,10-*Triphenylthioxanthenium Tetrafluoroborate* (**24**) *with Phenyl-lithium.*—Phenyl-lithium (1.05M; 9.3 ml) was added to a suspension of (**24**) (500 mg, 0.97 mmol) in dry THF (10 ml) at −30 to −40 °C under nitrogen. The reaction mixture was stirred for 3 h at that temperature and for 10 h at room temperature, and then worked up as mentioned above. The products were separated by preparative t.l.c. on silica gel using hexane as eluant to give 9,9-diphenylthioxanthene (**12**) (30 mg, 9%), biphenyl-2-yl(diphenyl)-*o*-(phenylthio)phenylmethane (**40**) (275 mg, 56%), 9,9-diphenylfluorene (**41**) (63 mg, 20.5%), and diphenyl sulphide (**42**) (30 mg, 17%). Compound (**40**), colourless prisms from hexane, m.p. 167 °C; δ 6.5—6.85 and 7.1—8.0 (28 H, m, ArH) (Found: C, 88.1; H, 5.6. $C_{37}H_{28}S$ requires C, 88.1; H, 5.6%). Compound (**41**), colourless prisms from hexane, m.p. 224 °C; δ 7.2 (10 H, s, 2 × Ph) and 7.25—7.85 (8 H, m, ArH) (Found: C, 93.9; H, 5.45. Calc. for $C_{25}H_{18}$: C, 94.3; H, 5.7%). An authentic sample of the fluorene (**41**) was synthesized by a known method.[18] Compounds (**12**), (**41**), and (**42**) were identical with authentic samples (i.r., n.m.r., and mixed m.p.).

9-*Biphenyl*-2-*ylthioxanthene* 10-*Oxide* (**43**).—*m*-Chloroperbenzoic acid (85%; 1.6 g) was added to an ice-cold stirred solution of compound (**11**) (3 g) in dichloromethane (30 ml). After being stirred for 24 h, the reaction mixture was neutralised with 5% aqueous sodium hydrogen carbonate and extracted with dichloromethane. The extract was dried ($MgSO_4$) and evaporated. The residue was recrystallised from dichloromethane–ether to give colourless plates (2.6 g, 81%), m.p. 191—193 °C (decomp.); $\nu_{max.}$ 1 035 cm^{-1} (S–O); δ 6.05 (1 H, s, 9-H), 6.75—7.1 (2 H, m, 1,8-H), 7.1—7.8 (13 H, m, ArH), and 7.88—8.13 (2 H, m, 4,5-H) (Found: C, 81.9; H, 4.95. $C_{25}H_{18}OS$ requires C, 81.9; H, 4.95%). The stereochemistry of the 9-biphenyl-2-yl and 10-sulphinyl groups was assigned as 9*eq*,10*ax* on the basis of the upfield shift of 1,8-H and the lowfield shift of 9-H.[11]

9-*Biphenyl*-2-*yl*-9-*phenylthioxanthene* (**46**).—Sodium hydride (60% in mineral oil; 50 mg) was added to a stirred suspension of compound (**23**) (500 mg) under nitrogen. The mixture was refluxed for 3 h, cooled, quenched with water, and extracted with dichloromethane. The extract was dried ($MgSO_4$) and concentrated. The residue was recrystallised from dichloromethane–hexane to give colourless prisms (366 mg, 88%), m.p. 155—157 °C; δ 6.15—6.5 (2 H, m, 2,6-H of 9*ax*-Ph), and 6.5—7.4 (20 H, m, ArH) (Found: C, 87.4; H, 5.2. $C_{31}H_{22}S$ requires C, 87.3; H, 5.2%).

Biphenyl-2-*yl*(*triphenyl*)*methane* (**47**).—A suspension of the thioxanthene (**46**) (450 mg) and Raney–Ni (W-2) (10 g) in ethanol (20 ml) was stirred and refluxed for 1 day. The catalyst was filtered off and the filtrate was evaporated. The residue was subjected to preparative t.l.c. on silica gel using dichloromethane–hexane (1:10) as eluant to give biphenyl-2-yl(triphenyl)methane (**47**) (175 mg, 42%) and the starting material (**46**) (204 mg). Recrystallisation of compound (**47**) from dichloromethane–hexane afforded colourless prisms, m.p. 184—185 °C; δ 6.1—6.4 (2 H, m, ArH), 6.6—6.85 (2 H, m, ArH), 7.07 (16 H, m, ArH), and 7.15—7.55 (4 H, m, ArH) (Found: C, 93.7; H, 6.2. $C_{31}H_{24}$ requires C, 93.9; H, 6.1%).

Desulphurisation of Compound (**40**).—A suspension of the ring-opened product (**40**) (210 mg) and Raney–Ni (W-2) (10 g) in ethanol (20 ml) was stirred and refluxed for 1 day. The reaction mixture was worked up as above. The residual solid was recrystallised from dichloromethane–hexane to give colourless prisms (132 mg, 80%), m.p. 185—186 °C; δ 6.1—6.85 (2 H, m, ArH), 7.08 (16 H, s, ArH), and 7.15—7.55 (4 H, m, ArH) (Found: C, 93.9; H, 6.1. $C_{31}H_{24}$ requires C, 93.9; H, 6.1%). The compound was identical with an authentic sample of (**47**) derived from (**46**) (mixed m.p., i.r., and ^1H n.m.r. spectra).

Reaction of 10-*Phenyl*-9-(p-*tolyl*)*thioxanthenium Tetrafluoroborate* (**22**) *with Phenyl-lithium.*—Phenyl-lithium (1.1M; 5.0 ml) was added to a stirred suspension of the sulphonium salt (**22**) (500 mg, 1.1 mmol) in dry ether (20 ml) at room temperature under nitrogen. The reaction mixture was stirred for 2 h at room temperature and then decomposed with water. The organic layer was separated and the aqueous layer was extracted with ether. The extracts were dried ($MgSO_4$) and evaporated under reduced pressure. The residual solid was subjected to preparative t.l.c. using hexane–benzene (10:1) as eluant to give 9-phenyl-9-(*p*-tolyl)thioxanthene (**48**). Recrystallisation from dichloromethane–hexane afforded colourless prisms (360 mg, 89%), m.p. 164—165 °C; δ 2.28 (3 H, s, Me) and 6.5—7.6 (17 H, m, ArH) (Found: C, 85.6; H, 5.5. $C_{26}H_{20}S$ requires C, 85.7; H, 5.5%).

Reaction of (**22**) *with* p-*Tolyl-lithium.*—*p*-Tolyl-lithium (1.0M; 5.5 ml) was added to a stirred suspension of the sulphonium salt (**22**) in dry ether (10 ml) at room temperature under nitrogen. The reaction mixture was stirred for 2 h at room temperature and then worked up as mentioned above. A mixture of 9-phenyl-9-(*p*-tolyl)thioxanthene (**48**) and 9,9-di(*p*-tolyl)thioxanthene (**49**) was obtained (395 mg) and the product ratio [(**48**):(**49**) = 2.4:1] was determined by the intensities of the methyl group and aromatic protons.

Reaction of 10-*Phenyl*-9-(p-*tolyl*)-10-*thia-anthracene* (**50**) *with* p-*Tolyl-lithium.*—A solution of lithium di-isopropylamide was prepared from a solution of di-isopropylamine (350.5 μl) in dry THF (10 ml) and butyl-lithium (15% in hexane; 1.25 ml) at 0 °C.[19] The sulphonium salt (**22**) (500 mg) was added to the solution of lithium di-isopropylamide at −55 °C. The resulting red solution of 10-phenyl-9-(*p*-tolyl)-10-thia-anthracene (**50**) was stirred for 2 h at that temperature and then *p*-tolyl-lithium (1.0M; 5.5 ml) in ether was added to the solution. After being stirred for 2 h the reaction mixture was gradually warmed to room temperature and worked up as mentioned above. The product was subjected to preparative t.l.c. on silica gel using benzene–hexane (1:10) as eluant to give 9-phenyl-9-(*p*-tolyl)thioxanthene (**48**) (273 mg, 68%). The mass spectrum of the crude product showed no peak at *m/z* 378 due to 9,9-di(*p*-tolyl)thioxanthene (**49**).

9-*Benzoyl*-10-*phenyl*-10-*thia-anthracene* (**52**).—Sodium hydride (60% in mineral oil; 155 mg) was added to a suspension of the sulphonium salt (**20**) (1.5 g) in dry THF (100 ml) at 0 °C under nitrogen. The reaction mixture was stirred at 0 °C for 3 h and evaporated under reduced pressure. Water was added to the oily residue and the mixture was extracted with dichloromethane (2 × 20 ml). The extract was dried ($MgSO_4$) and evaporated under reduced pressure. The residual solid was recrystallised from dichloromethane–ether to afford orange prisms (965 mg, 79.5%), m.p. 137—138 °C (decomp.); $\nu_{max.}$ 1 540—1 480 cm^{-1} (ylide CO); δ 6.75—7.4 (14 H, m, ArH), 7.64 (2 H, dd, *J* 7.5, 1.5 Hz, 4,5-H), and 8.20 (2 H, dd, *J* 7.5, 1.5 Hz) (Found: C, 82.5; H, 4.85. $C_{26}H_{18}OS$ requires C, 82.5; H, 4.8%).

Thermal Rearrangement of Compound (**52**).—A solution of the thia-anthracene (**52**) (100 mg) in dry benzene (20 ml) was stirred and refluxed for 3 h under nitrogen. The orange-brown

solution faded within 30 min and was then evaporated under reduced pressure. The residual solid was recrystallised from chloroform–hexane to give 9-benzoyl-9-phenylthioxanthene (**53**) quantitatively as colourless plates, m.p. 198 °C (decomp.); $\nu_{max.}$ 1 675 cm^{-1} (CO); δ 7.65 (2 H, dd, *J* 7.5, 2.0 Hz, ArH) and 6.65 (16 H, m, ArH) (Found: C, 82.7; H, 4.8. $C_{26}H_{18}OS$ requires C, 82.5; H, 4.8%). The sample was identical with an authentic sample synthesized in a different way.

9-*Benzoyl*-9-*phenylthioxanthene* (**53**).—An ethereal solution of butyl-lithium (1M; 4 ml) was added to a stirred solution of 9-phenylthioxanthene (**13**) (1 g) in dry ether (15 ml) at 0 °C under nitrogen. The reaction mixture was stirred at room temperature for 2 h after which a solution of 2-(benzoylthio)pyridine [17] (0.8 g) in dry benzene (2 ml) was added to it at 0 °C. Stirring was continued for 30 min at that temperature and then for 1 h at room temperature. The red solution did not fade and benzoyl chloride (0.462 ml) was added to the solution. After being stirred at room temperature for 3 h the reaction mixture was poured into water. The organic layer was separated and the aqueous layer was extracted with chloroform. The extract was dried ($MgSO_4$) and evaporated. The residue was chromatographed on silica gel using hexane and hexane–benzene (1:1) as eluant. The starting material (**13**) (300 mg) was recovered from the hexane fraction and the product (**53**) (850 mg, 62%) was isolated from the hexane–benzene (1:1) fraction. Recrystallisation of the thioxanthene (**53**) from chloroform–hexane gave colourless plates, m.p. 198 °C; $\nu_{max.}$ 1 675 cm^{-1} (CO); δ 7.65 (2 H, dd, *J* 7.5, 2.0 Hz) and 7.5—6.65 (16 H, m, ArH) (Found: C, 82.3; H, 4.7. $C_{26}H_{18}OS$ requires C, 82.5; H, 4.8%).

Reaction of Compound (**52**) *with* p-*Tolyl-lithium*.—An ethereal solution of *p*-tolyl-lithium (0.8M; 2.5 ml) was added to a suspension of compound (**52**) in dry THF (15 ml) at 0 °C under nitrogen. The reaction mixture was stirred for 3 h and decomposed with aqueous ammonium chloride. The organic layer was separated and the aqueous layer was extracted with benzene. The extract was dried ($MgSO_4$) and evaporated to dryness. The residue was subjected to preparative t.l.c. on silica gel using benzene–hexane (1:1) as eluant to give 9-benzoylthioxanthene (**4**) (245 mg, 81%) and a mixture of biphenyl derivatives. Mass spectrum of the mixture showed two molecular ion peaks at *m/z* 182 due to bi-*p*-tolyl and *m/z* 168 due to 4-methylbiphenyl (**54**). The compound (**54**) was identified with an authentic sample by high performance liquid chromatography on μ-Fine SIL-C_{18} using acetonitrile–water (7:3) as eluant.

References

1 (*a*) C. C. Price, M. Hori, T. Parasaran, and M. Polk, *J. Am. Chem. Soc.*, 1963, **85**, 2278; (*b*) M. Hori, M. Nozaki, and T. Kataoka, *Yakugaku Zasshi*, 1974, **84**, 466.
2 (*a*) M. Hori, T. Kataoka, H. Shimizu, and C.-F. Hsu, *Chem. Lett.*, 1973, 391; (*b*) M. Hori, T. Kataoka, and H. Shimizu, *ibid.*, 1974, 1117.
3 (*a*) G. H. Senkler, Jr., J. Stackhouse, B. E. Maryanoff, and K. Mislow, *J. Am. Chem. Soc.*, 1974, **96**, 5648; (*b*) B. E. Maryanoff, J. Stackhouse, G. H. Senkler, Jr., and K. Mislow, *ibid.*, 1975, **97**, 2718.
4 A. G. Hortmann, R. L. Harris, and J. A. Miles, *J. Am. Chem. Soc.*, 1974, **96**, 6119.
5 M. Hori, T. Kataoka, H. Shimizu, Y. Itagaki, and T. Higuchi, *Tetrahedron Lett.*, 1979, 1603; M. Hori, T. Kataoka, H. Shimizu, M. Ban, and H. Matsushita, *J. Chem. Soc., Perkin Trans. 1*, 1987, 187.
6 C. C. Price and J. Follweiler, *Heterocycles*, 1978, **11**, 219.
7 R. R. Burtner and J. W. Cusic, *J. Am. Chem. Soc.*, 1943, **65**, 1582.
8 J. W. Crivello and J. H. W. Lam, *J. Org. Chem.*, 1978, **43**, 3055.
9 M. Hori, T. Kataoka, H. Shimizu, and S. Ohno, *Heterocycles*, 1979, **12**, 1555; S. Ohno, H. Shimizu, T. Kataoka, and M. Hori, *J. Org. Chem.*, 1984, **49**, 3151.
10 A. L. Ternay, Jr., J. Hermann, and S. A. Evans, *J. Org. Chem.*, 1969, **34**, 940; A. L. Ternay and S. A. Evans, *ibid.*, 1974, **39**, 2941; S. A. Evans and A. L. Ternay, Jr., *ibid.*, 1975, **40**, 2993.
11 M. Hori, T. Kataoka, H. Shimizu, and S. Ohno, *Heterocycles*, 1979, **12**, 1417; S. Ohno, H. Shimizu, T. Kataoka, and M. Hori, *Chem. Pharm. Bull.*, 1984, **32**, 3471.
12 T. Takemura, K. Tokita, S. Kondo, and N. Mori, *J. Chem. Res.*, 1978 (*S*), 452.
13 M. Hori, T. Kataoka, H. Shimizu, and M. Miyagaki, *Chem. Pharm. Bull.*, 1974, **22**, 2004.
14 M. M. Urberg and E. T. Kaiser, *J. Am. Chem. Soc.*, 1967, **89**, 5931.
15 S. Ohno, H. Shimizu, T. Kataoka, and M. Hori, *J. Org. Chem.*, 1984, **49**, 2472.
16 H. Kato, K. Tanaka, and M. Ohta, *Bull. Chem. Soc. Jpn.*, 1966, **39**, 1248; T. Mukaiyama, M. Araki, and H. Takei, *J. Am. Chem. Soc.*, 1973, **95**, 4763.
17 F. M. Beringer, R. A. Falk, M. Karniol, I. Lillien, G. Masulio, M. Mausner, and E. Sommer, *J. Am. Chem. Soc.*, 1959, **81**, 342.
18 H. Hart and E. A. Sedor, *J. Am. Chem. Soc.*, 1967, **89**, 2342; R. A. Abramovitch and E. P. Kyba, *ibid.*, 1974, **96**, 480.
19 I. Fleming and I. Paterson, *Synthesis*, 1979, 736.

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