Reactivities of Heteroaromatic Cations containing a Group VIB Element in Nucleophilic Reactions. Reactions of 9-Phenyl-xanthylium, -thioxanthylium, and -selenoxanthylium Salts with Amines, Sodium Phenolate, and Sodium Benzenethiolate

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Reactions of 9-phenylchalcogenoxanthylium salts (**1a**—**c**) with some nucleophiles have been examined in order to find the differences in reactivity in nucleophilic reactions. The chalcogenoxanthylium salts (**1a**—**c**) react with aniline in ether to give 9-anilino-9-phenylchalcogenoxanthenes (**7a**—**c**). However, in acetonitrile the xanthylium salt (**1a**) affords *N*,4-bis(9-phenylxanthen-9-yl)aniline (**9a**) together with the anilinoxanthene (**7a**) (at room temperature) or 9-(*p*-aminophenyl)-9-phenylxanthene (**8a**) (at reflux) and the sulphur (**1b**) and the selenium derivative (**1c**) affords only the anilino derivatives (**7b,c**), respectively.

In the reactions with sodium phenolate, the thioxanthylium salt (**1b**) gave 9-phenoxy-9-phenylthioxanthene (**13b**), whereas the oxygen (**1a**) and the selenium congener (**1c**) gave *O*,4-bis(9-phenylchalcogenoxanthen-9-yl)phenols (**15a,c**) together with the 9-phenoxy derivatives (**13a,c**), respectively.

The results show that the thioxanthylium salt (**1b**) gave the products formed on attack by the heteroatom of the ambident nucleophiles and the ratio of the carbon attack increased in the order (**1a**) > (**1c**) > (**1b**). This difference would be attributable to the properties of carbocations at the 9-position in the heteroaromatic cations (**1a**—**c**).

We have investigated the reactivities of the 9-phenylxanthylium salt (**1a**) and its sulphur (**1b**) and selenium (**1c**) analogues not only experimentally but also theoretically. In the electrophilic reaction (nitration) the thioxanthylium salt (**1b**) and its selenium congener (**1c**) yielded the dinitrated products under the conditions where the oxygen congener (**1a**) afforded the mononitrated products.[1,2] On the other hand, in the nucleophilic reaction (reaction with active methylene compounds), these cations (**1a**—**c**) reacted with the nucleophiles exclusively at the 9-position (C-9) and no difference was found in their reaction modes.[3] Molecular-orbital calculations show that the reaction indices for the nucleophilic substitution reaction at C-9 of the cations (**1a**—**c**) are larger than those at the other positions,[3] therefore the nucleophilic substitution is not expected to occur at positions other than C-9. We therefore sought molecules containing different nucleophilic sites which could attack C-9 of the cations (**1a**—**c**). The present report describes the reactions of the heteroaromatic cations (**1a**—**c**) with some amines, sodium phenolate, and sodium benzenethiolate.

Reactions with Amines.—Reactions of the 9-phenylxanthylium (**1a**) and thioxanthylium (**1b**) salts with aliphatic and aromatic amines are shown in Scheme 1. Aliphatic amines attacked C-9 of the cations (**1a,b**) to give the *N*-chalcogenoxanthenylamines (**2**)—(**4**), whereas aniline and the *N*-substituted anilines reacted through the nitrogen atom, and at the *para*-carbon atom of the benzene ring, respectively. Products and yields are summarized in Table 1. This finding indicates that the anilines act as ambident nucleophiles. We further studied the reactions of the heteroaromatic compounds (**1a**—**c**) including the selenium analogue (**1c**) with aniline and the results are shown in Table 2. The 9-anilino derivatives (**7a**—**c**) were obtained from the reactions in ether. The reaction of the oxygen derivative (**1a**) in acetonitrile at room temperature afforded *N*,4-bis(9-phenylxanthen-9-yl)aniline (**9a**) in 78.5% yield

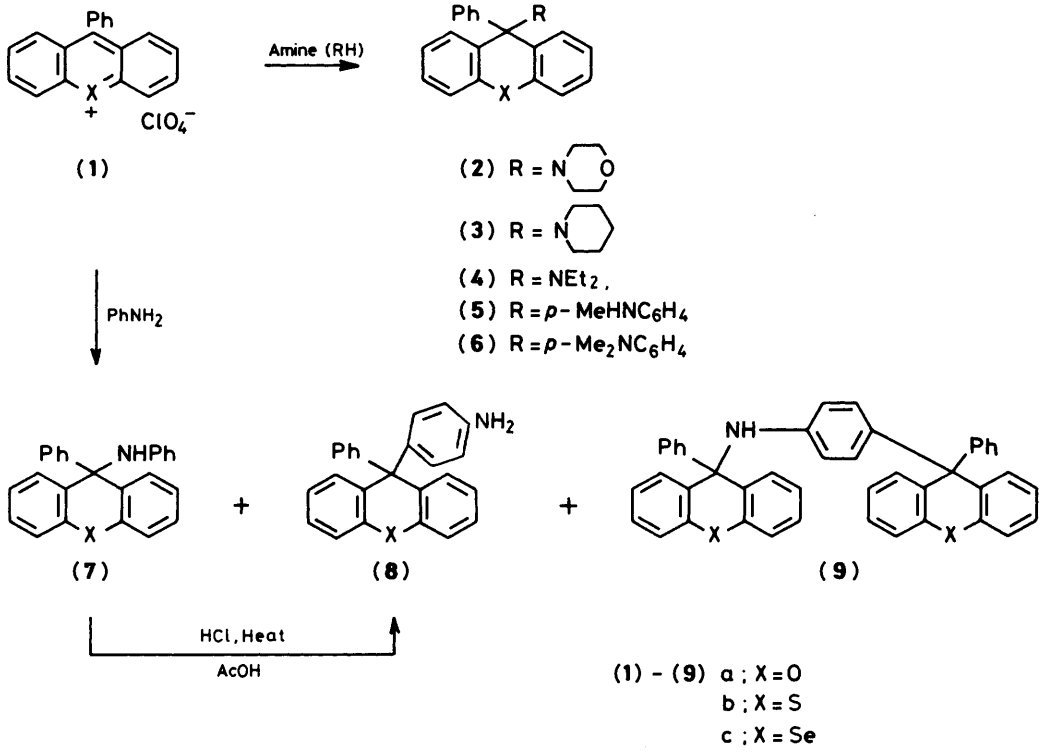
Table 1. Reactions of 9-phenyl-xanthylium (**1a**) and -thioxanthylium (**1b**) salts with amines in ether

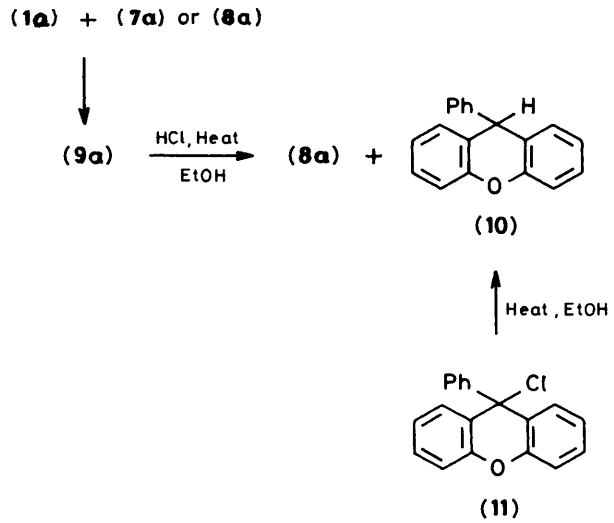
Amine	Product(%) from (**1a**)	Product(%) from (**1b**)
Morpholine	(**2a**) (95.5)	(**2b**) (92)
Piperidine	(**3a**) (92)	(**3b**) (93)
Diethylamine	(**4a**) (91)	(**4b**) (93)
N-Methylaniline	(**5a**) (95)	(**5b**) (97)
N,*N*-Dimethylaniline	(**6a**) (94)	(**6b**) (98)

Table 2. Reactions of the chalcogenoxanthylium salts (**1a**—**c**) with aniline

Reaction conditions	Product(%) from (**1a**)	Product(%) from (**1b**)	Product(%) from (**1c**)
Ether (room temp.)	(**7a**) (89)	(**7b**) (91)	(**7c**) (92)
Acetonitrile (room temp.)	(**7a**) (11.5), (**9a**) (78.5)	(**7b**) (98)	(**7c**) (98)
Acetonitrile (50 °C)	(**8a**) (27), (**9a**) (65)	(**7b**) (88.5)	(**7c**) (89)
Acetic acid (room temp.)	(**8a**) (2), (**9a**) (95)	(**7b**) (72)	(**7c**) (96)
Acetic acid (reflux)	(**8a**) (99)	(**8b**) (91.5)	(**8c**) (94)

together with the *N*-alkylated product (**7a**). The *N*,4-disubstituted aniline (**9a**) was also obtained in acetonitrile at 50 °C or in acetic acid at room temperature. Under these conditions, the sulphur (**1b**) and selenium (**1c**) analogues afforded only 9-anilino derivatives (**7b**, **c**) in high yields, respectively. The anilino derivatives (**7a**—**c**) underwent the Hofmann–Martius rearrangement to afford the *p*-aminophenyl derivatives (**8a**—**c**) upon being heated with hydrochloric acid in acetic acid. The 9-(*p*-aminophenyl) derivatives (**8a**—**c**) were directly obtained upon refluxing the chalcogenoxanthylium salts (**1a**—**c**) with aniline in acetic acid. The bis(chalcogenoxanthenyl)anilines (**9a**—**c**) were formed in high yields when the chalcogenoxanth-





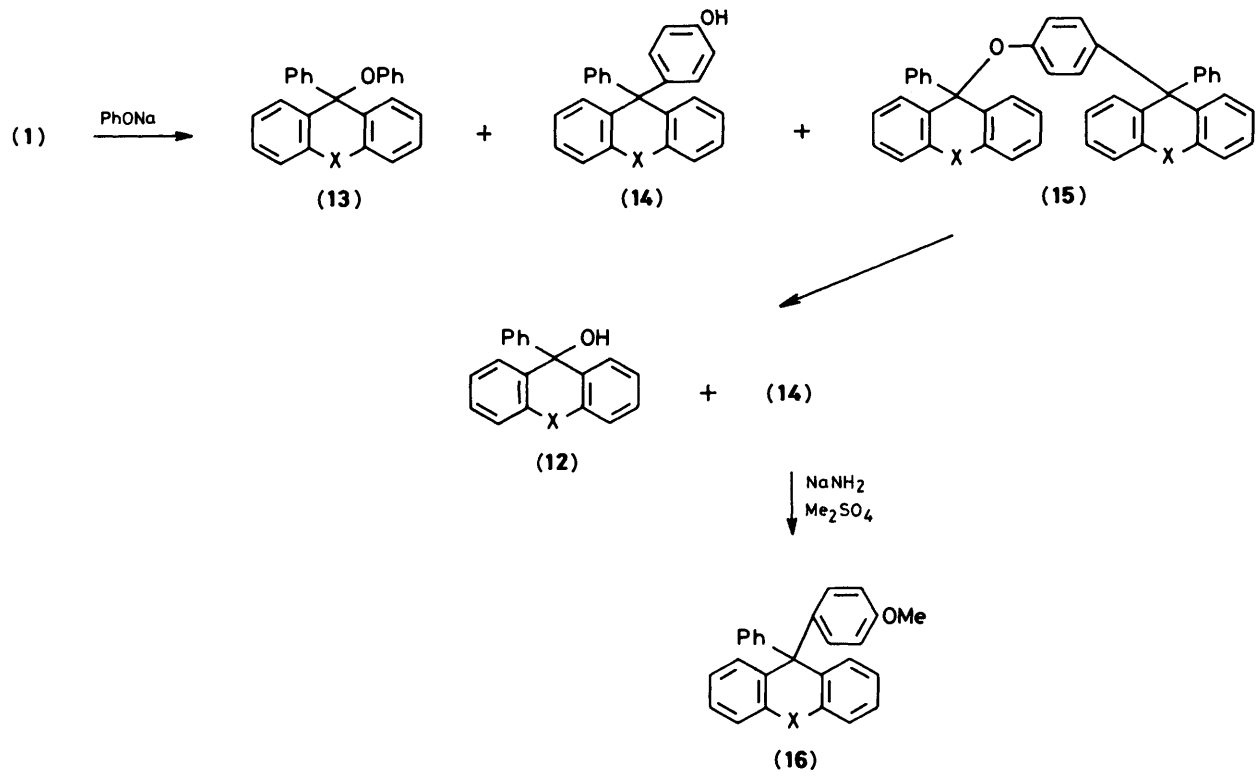
Scheme 1.

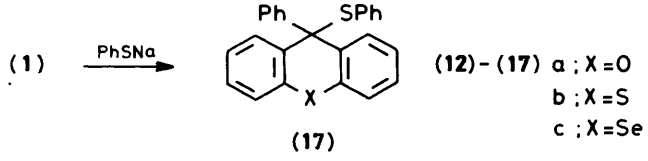
ylium salts (**1a**—**c**) were refluxed in acetonitrile with 0.5 equiv. of aniline in the presence of potassium carbonate. Furthermore, the *N*,4-bisxanthenylaniline (**9a**) was formed from the reaction of the xanthylium salt (**1a**) with the anilinoxanthene (**7a**) or the *p*-aminophenylxanthene (**8a**). In order to elucidate the structures of the *N*,4-disubstituted anilines (**9**), the oxygen derivative (**9a**) was decomposed with hydrochloric acid in ethanol to give 9-(*p*-aminophenyl)-9-phenylxanthene (**8a**) and an unexpected product, 9-phenylxanthene (**10**). We had expected the formation of 9-chloro-9-phenylxanthene (**11**) or its hydrolysis product, 9-phenylxanthen-9-ol (**12**), but these compounds were not isolated. The formation of the xanthene (**10**) was rationalized by the fact that the 9-chloroxanthene (**11**) was reduced to the xanthene (**10**) in ethanol under reflux.

Table 3. Reactions of the chalcogenoxanthylium salts (**1a**—**c**) with sodium phenolate

Reaction conditions	Product(%) from (**1a**)	(**1b**)	(**1c**)
Tetrahydrofuran (room temp.)	(**13a**) (15.5), (**15a**) (66)	(**13b**) (74)	(**13c**) (17.5), (**15c**) (58)
Acetonitrile (room temp.)	(**13a**) (55), (**15a**) (23)	(**13b**) (88)	(**13c**) (89)
Phenol (50 °C)	(**14a**) (96)	(**14b**) (91.5)	(**14c**) (93.5)

Reactions with Sodium Phenolate.—The phenolate anion is a well-known ambident nucleophile. We next investigated the reactions of the cations (**1a**—**c**) with sodium phenolate as shown in Scheme 2 and Table 3. The thioxanthylium salt (**1b**) afforded 9-phenoxy-9-phenylthioxanthene (**13b**) in high yields from the reaction in dry tetrahydrofuran or acetonitrile, while the oxygen (**1a**) or the selenium analogue (**1c**) afforded the *O*,4-bis(9-phenylxanthen-9-yl)phenol (**15a**) or the corresponding selenium compound (**15c**) in addition to the *O*-alkylated phenol (**13a**) or (**13c**). In phenol, all of the cations (**1a**—**c**) gave the *C*-alkylated phenols (**14a**—**c**). This finding can be explained by the selective solvation[4] arising from hydrogen bonding between the hydroxy group of phenol and the phenolate anion which causes the nucleophilicity of the anionic oxygen to be depressed. Structures of *O*,4-bisalkylated phenols (**15a**—**c**) were determined by the acidic hydrolysis. Compounds (**15a**—**c**) were acid-labile and were converted into the 9-phenyl-9-(*p*-hydroxyphenyl)xanthene derivatives (**14a**—**c**) and 9-phenylxanthen-9-ol derivatives (**12a**—**c**) by preparative t.l.c. using silica gel or by treatment with hydrogen chloride. The 9-(*p*-hydroxyphenyl) compounds (**14a**—**c**) were methylated with sodium amide and dimethyl sulphate to give the 9-(*p*-methoxyphenyl)xanthene derivatives (**16a**—**c**), which were identical with the authentic specimens.[5]





Scheme 2.

Reactions with Sodium Benzenethiolate.—The chalcogenoxanthylium salts (**1a**—**c**) were allowed to react with sodium benzenethiolate. In all cases the thiolate anion attacked at C-9 of the salts (**1a**—**c**) to afford 9-phenyl-9-(phenylthio)chalcogenoxanthenes (**17a**—**c**). Nucleophilic attack did not occur through the carbon atoms of the benzene ring of the phenolate anion, probably because the anionic sulphur is much more nucleophilic than the aromatic carbons.

Discussion

It was found that the 9-phenylxanthylium salt (**1a**), the sulphur (**1b**) and the selenium analogue (**1c**) behave differently towards nucleophiles. These facts can be explained by the stability–selectivity relationship of carbocations. Swain *et al.*[6] and Sneen *et al.*[7] have studied the reactivities of carbocations towards nucleophiles and have showed that the more stable the carbocations, the higher their selectivity. A similar relationship was found in the deuteriation of the cumenyl anion. The cumenyl anion was deuteriated only at the α-position with D_2O, while it reacted with DCl not only at the α-position (50—70%) but also at the *ortho*- (3—5%) and *para*-positions (10—20%).[8] In the reactions of the t-butyl or trityl cation with phenolate anion, the former underwent *O*-alkylation (25%) and *C*-alkylation (75%), while the latter underwent *O*-alkylation (95%) and *C*-alkylation (5%).[9] These findings show that the ratio of *O*-alkylation increases with the stability of the carbocations. *C*-Alkylation of the phenolate anion is not energetically feasible owing to the loss of aromaticity (formation of the *ortho*- or *para*-quinoid σ-complex). The reaction between the thioxanthylium cation (**1b**) and aniline resulted in *N*-alkylation, while the oxygen (**1a**) and the selenium (**1c**) analogues underwent both *N*- and *C*-alkylation under the same conditions. Furthermore, in the reactions with sodium phenolate the sulphur analogue (**1b**) caused only *O*-alkylation and the proportion of *C*-alkylation increased in the order (**1b**) < (**1c**) < (**1a**). In other words, *C*-alkylation decreases in the order $-O^+=$ (**1a**) > $-Se^+=$ (**1c**) > $-S^+=$ (**1b**). Consequently the stability of the xanthylium salts is (**1b**) > (**1c**) > (**1a**). This order is different from that of the atomic number in the periodic table. A similar observation has been reported for the p*K*a values of the chalcogenopyrylium, benzopyrylium, and dibenzo[*b*,*d*]pyrylium cations.[10] However, the p*K*a values of the chalcogenoxanthylium salts are abnormal [xanthylium ion (−0.83), thioxanthylium ion (−0.21), and selenoxanthylium ion (−1.67)] and the selenium derivative is the least stable to base.[10] These data are not consistent with our experimental results described above and our data derived from molecular orbital calculations.[3]

Experimental

M.p.s were determined on a Yanagimoto micro-melting point apparatus and are uncorrected. I.r. spectra (KBr) were recorded on a JASCO A-1 spectrophotometer. N.m.r. spectra were obtained for solutions in $CDCl_3$ on a Hitachi R-20B spectrometer with tetramethylsilane as an internal standard.

General Procedures for Reactions of the Chalcogenoxanthylium Salts (**1a**,**b**) *with Amines in Ether.*—The 9-phenylxanthylium (**1a**) or thioxanthylium salt (**1b**) (1.00 g) was added in portions to a solution of an amine (6 mol equiv.) in dry ether (35 ml) and the reaction mixture was stirred for 2 h at room temperature. Aqueous $NaHCO_3$ was added to the mixture and the organic layer was separated. The aqueous layer was extracted with benzene. The organic layer and the extracts were

Table 4. Physical properties of compounds (**2**)—(**17**)

Compd.	Appearance[a] (recrystallisation solvents)	M.p. (°C)	Formula	Calc. for (%) C	H	N	Found (%) C	H	N
(**2a**)	Prisms (benzene–light petroleum)	193—194	$C_{23}H_{21}NO_2$	80.4	6.2	4.1	80.55	6.3	4.2
(**2b**)	Needles (ether)	173—174	$C_{23}H_{23}NOS$	76.8	5.9	3.9	76.6	6.1	3.8
(**3a**)	Prisms (benzene–light petroleum)	169—170	$C_{24}H_{23}NO$	84.4	6.8	4.1	84.4	6.9	4.2
(**3b**)	Plates (ether)	141—142	$C_{24}H_{23}NS$	80.6	6.5	3.9	80.3	6.3	3.85
(**4a**)	Prisms (light petroleum)	105	$C_{23}H_{23}NO$	83.85	7.0	4.25	84.1	7.1	4.4
(**4b**)	Plates (ether)	109	$C_{23}H_{23}NS$	79.95	6.7	4.1	79.8	6.6	3.9
(**5a**)	Prisms (benzene–EtOH)	183—185	$C_{26}H_{21}NO$	85.9	5.8	3.9	85.75	6.0	3.8
(**5b**)	Prisms (MeOH)	208—210	$C_{26}H_{21}NS$	82.3	5.6	3.7	82.4	5.5	3.6
(**6a**)	Prisms (benzene–EtOH)	198—200	$C_{27}H_{23}NO$	85.9	6.1	3.7	85.8	6.15	3.7
(**6b**)	Prisms (ether)	228—230	$C_{27}H_{23}NS$	82.4	5.9	3.6	82.7	6.2	3.3
(**7a**)	Plates (benzene–EtOH)	183—184	$C_{25}H_{19}NO$	85.9	5.5	4.0	85.8	5.55	3.9
(**7b**)	Plates (benzene–light petroleum)	238—239	$C_{25}H_{19}NS$	82.15	5.2	3.8	82.4	5.2	3.7
(**7c**)	Prisms (benzene–hexane)	255—257	$C_{25}H_{19}NSe$	72.8	4.65	3.4	72.8	4.6	3.3
(**8a**)	Prisms (EtOH)	232—234	$C_{25}H_{19}NO$	85.9	5.5	4.0	85.7	5.7	3.9
(**8b**)	Prisms (EtOH)	195—196	$C_{25}H_{19}NS$	82.15	5.2	3.8	81.9	5.3	3.9
(**8c**)	Prisms (benzene–light petroleum)	187—188	$C_{25}H_{19}NSe$	72.8	4.65	3.4	72.9	4.7	3.7
(**9a**)	Fine needles (xylene)	>300	$C_{44}H_{31}NO_2$	87.25	5.2	2.3	87.3	5.3	2.6
(**9b**)	Fine needles (benzene)	295—297	$C_{44}H_{31}NS_2$	82.8	4.9	2.2	82.8	5.3	2.1
(**9c**)	Fine needles (benzene)	278—279	$C_{44}H_{31}NSe_2$	72.2	4.3	1.9	72.3	4.5	2.1
(**13b**)	Prisms (benzene–light petroleum)	164—165	$C_{25}H_{18}OS$	81.9	4.95		81.8	5.05	
(**13c**)	Prisms (benzene–light petroleum)	139—140	$C_{25}H_{18}OSe$	72.6	4.4		72.65	4.45	
(**14a**)	Prisms (benzene–light petroleum)	173—174	$C_{25}H_{18}O_2$	85.6	5.3		85.7	5.2	
(**14b**)	Prisms (benzene–light petroleum)	230—231	$C_{25}H_{18}OS$	81.95	4.95		82.0	5.1	
(**14c**)	Needles (benzene–light petroleum)	225—226	$C_{25}H_{18}OSe$	72.6	4.4		72.4	4.4	
(**15a**)	Needles (benzene)	273—274 (decomp.)	$C_{44}H_{30}O_3$	87.1	5.0		86.75	5.2	
(**15c**)	Needles (benzene)	247—249 (decomp.)	$C_{44}H_{30}OSe_2$	72.1	4.1		71.95	4.2	
(**17a**)	Prisms (benzene–light petroleum)	174—175	$C_{25}H_{18}OS$	81.9	4.95		82.0	5.0	
(**17b**)	Prisms (benzene–light petroleum)	158—159	$C_{25}H_{18}S_2$	78.5	4.7		78.5	4.7	
(**17c**)	Prisms (benzene–light petroleum)	153—154	$C_{25}H_{18}SSe$	69.9	4.3		69.8	4.2	

[a] All the compounds were colourless crystals.

combined, dried ($MgSO_4$), and evaporated, and the residue was recrystallised. The physicochemical and analytical data of the products are shown in Table 4 and their spectral data are summarized in Table 5.

Reactions of the Chalcogenoxanthylium Salts (**1a**—**c**) *with Aniline.*—The chalcogenoxanthylium salt (**1**) (1.0 g) was added in portions to a solution of aniline (6 mol equiv.) in a solvent (35 ml). The reaction mixture was stirred for 2 h under the conditions cited in Table 2 and poured into water. The precipitate was collected, washed with 5% aqueous $NaHCO_3$ and then water, and was dried. In the case of the reaction in ether, the reaction mixture was treated with 5% aqueous $NaHCO_3$. The organic layer was separated and the aqueous layer was extracted with ether. The insoluble material was filtered off and dried. The organic layer and the extracts were combined, dried (K_2CO_3), and evaporated. The product was separated into an ether-soluble part and an ether-insoluble part. The ether-soluble part gave 9-anilino derivatives (**7**) or 9-(*p*-aminophenyl) derivatives (**8**), and the ether-insoluble part gave *N*,4-bis(9-phenylxanthen-9-yl)aniline (**9a**). Products and yields are listed in Table 2 and their physicochemical and spectral data are summarized in Tables 4 and 5, respectively.

Rearrangement of the Anilinochalcogenoxanthenes (**7a**—**c**) *to* p-*Aminophenyl Derivatives* (**8a**—**c**).—A mixture of the anilino compound (**7**) (1.5 mmol) and concentrated hydrochloric acid (1.5 ml) in acetic acid (30 ml) was heated in a water bath for 4 h and the solvent was removed under reduced pressure. The residue was washed with aqueous $NaHCO_3$ and then water, and was dried ($MgSO_4$). Recrystallisation of the residue from ethanol gave colourless prisms. The products, 9-*p*-aminophenyl-9-phenyl-xanthene (**8a**) (71%), -thioxanthene (**8b**) (73%), and -selenoxanthene (**8c**) (71%), were identical with those obtained above.

N,4-*Bis*(9-*phenylchalcogenoxanthen*-9-*yl*)*anilines* (**9a**—**c**).—Aniline (0.5 mol equiv.) was added to a solution of the chalcogenoxanthylium salt (**1**) (1.0 g) in dry acetonitrile (30 ml) and the mixture was refluxed for 2 h. Anhydrous K_2CO_3 (0.2 g) was added to the mixture which was refluxed for a further 2 h. The cooled reaction mixture was poured into water. The precipitate was filtered off, washed with water, and dried. *N*,4-Bis(9-phenylxanthen-9-yl)aniline (**9a**) (93%), and the corresponding thioxanthene (**9b**) (91%) and selenoxanthene (**9c**) derivatives (83%) were obtained.

Formation of N,4-*Bis*(9-*phenylxanthen*-9-*yl*)*aniline* (**9a**) *from* 9-*Anilino*-9-*phenylxanthene* (**7a**) *or* 9-(p-*Aminophenyl*)-9-*phenylxanthene* (**8a**).—(*a*) 9-Phenylxanthylium perchlorate (**1a**) (0.82 g, 2 mmol) was added to a solution of the anilino compound (**7a**) (0.8 g, 2 mmol) in dry acetonitrile (25 ml) and the mixture was stirred for 2 h at room temperature. Water was added to the reaction mixture and the resulting precipitate was filtered off and dried ($MgSO_4$). The ether-insoluble part gave *N*,4-bisxanthen-9-ylaniline (**9a**) (0.62 g, 51%) and the ether-soluble part gave 9-phenylxanthen-9-ol (**12a**) (0.12 g, 11%).

(*b*) The xanthylium salt (**1a**) (0.30 g, 8.5 mmol) was gradually added to a solution of the aminophenyl derivative (**8a**) (0.30 g, 8.5 mmol) in dry acetonitrile (30 ml) and the mixture was stirred

Table 5. Spectral data of compounds (**2**)—(**17**)

Compd.	$\nu_{max.}$ (cm^{-1})	δ($CDCl_3$)
(**2a**)		1.90—2.85 (4 H, m, CH_2N), 3.45—3.80 (4 H, m, CH_2O), and 6.7—7.75 (13 H, m, ArH)
(**2b**)		2.34—2.60 (4 H, m, CH_2N), 3.54—3.80 (4 H, m, CH_2O), and 6.95—7.6 (13 H, m, ArH)
(**3a**)		1.15—1.75 (6 H, m, CH_2), 2.00—2.35 (4 H, m, CH_2N), and 6.9—7.75 (13 H, m, ArH)
(**3b**)		1.30—1.75 (6 H, m, CH_2), 2.25—2.65 (4 H, m, CH_2N), and 7.1—7.55 (13 H, m, ArH)
(**4a**)		0.85 (6 H, t, *J* 7.0 Hz, Me), 2.52 (4 H, q, *J* 7.0 Hz, CH_2), and 6.8—7.7 (13 H, m, ArH)
(**4b**)		0.90 (6 H, t, *J* 7.2 Hz, Me), 2.86 (4 H, q, *J* 7.2 Hz, CH_2), and 6.9—7.76 (13 H, m, ArH)
(**5a**)	3 480 (NH)	2.80 (3 H, s, Me), 6.56 (2 H, d, *J* 9.0 Hz, 3-ArH), 6.81 (2 H, d, *J* 9.0 Hz, 2-ArH), and 6.95—7.5 (13 H, m, ArH)
(**5b**)	3 360 (NH)	2.82 (3 H, s, Me), 6.54 (4 H, s, C_6H_4N), and 6.65—7.6 (13 H, m, ArH)
(**6a**)		2.90 (6 H, s, Me), 6.63 (2 H, d, *J* 7.0 Hz, 3-ArH), 6.90 (2 H, d, *J* 7.0 Hz, 2-ArH), and 6.95—7.5 (13 H, m, ArH)
(**6b**)		2.92 (6H, s, Me), 6.58 (4 H, s, C_6H_4N), and 6.65—7.6 (13 H, m, ArH)
(**7a**)	3 375 (NH)	4.48 (1 H, br s, NH) and 6.75—7.7 (18 H, m, ArH)
(**7b**)	3 300 (NH)	6.0 (1 H, br s, NH) and 6.35—7.88 (18 H, m, ArH)
(**7c**)	3 300 (NH)	6.25—7.95 (m, ArH)[a]
(**8a**)	3 400, 3 320 (NH_2)	3.55 (2 H, br s, NH_2), 6.52 (2 H, d, *J* 9.0 Hz, 3-ArH), 6.74 (2 H, d, *J* 9.0 Hz, 2-ArH), and 6.9—7.4 (13 H, m, ArH)
(**8b**)	3 425, 3 330 (NH_2)	3.5 (2 H, br s, NH_2), 6.55 (4 H, s, C_6H_4N), and 6.65—7.6 (13 H, m, ArH)
(**8c**)	3 435, 3 350 (NH_2)	3.20 (2 H, br s, NH_2), 6.56 (4 H, br s, C_6H_4N), 6.65—7.7 (13 H, m, ArH)
(**9a**)	3 350 (NH)	*b*
(**9b**)	3 350 (NH)	*b*
(**9c**)	3 375 (NH)	*b*
(**13b**)		6.45—7.70 (m, ArH)
(**13c**)		6.55—7.80 (m, ArH)
(**14a**)	3 550—3 075 (OH)	4.78 (1 H, br s, OH), 6.50—7.50 (17 H, m, ArH), 7.33 (C_6H_6)[c]
(**14b**)	3 550—3 050 (OH)	6.4—7.7 (17 H, m, ArH) and 8.9 (1 H, br s, OH)[a]
(**14c**)	3 525—3 050 (OH)	6.4—7.75 (17 H, m, ArH)[a]
(**17a**)		6.4—7.9 (18 H, m, ArH)
(**17b**)		6.75—7.85 (18 H, m, ArH)
(**17c**)		6.85—7.70 (18 H, m, ArH)

[a] The spectra were measured in a mixture of $CDCl_3$ and $(CD_3)_2SO$. [b] The compounds (**9a**—**c**) and (**15a**,**c**) were not sufficiently soluble in organic solvents. [c] The crystals contained the recrystallisation solvent, benzene.

for 2 h at room temperature. Water was added to the mixture and the precipitate was filtered off and dried ($MgSO_4$). The product was the *N*,4-bisxanthenylaniline (**9a**) (0.3 g, 75.5%).

Decomposition of N,4-*Bis*(9-*phenylxanthen*-9-*yl*)*aniline* (**9a**) *with Hydrochloric Acid.*—A mixture of the aniline (**9a**) (90.21 g) and concentrated hydrochloric acid (2 ml) in ethanol (40 ml) was refluxed for 1 h. The reaction mixture was concentrated under reduced pressure and the residual solid was dissolved in ether. The ether-soluble solid was identified as 9-phenylxanthene (**10**) (0.09 g, 49.5%). The ether-insoluble solid was treated with aqueous sodium hydroxide and extracted with ether. The extract was dried and evaporated to give 9-(*p*-aminophenyl)-9-phenylxanthene (**8a**) (0.13 g, 54%).

Reduction of 9-*Chloro*-9-*phenylxanthene* (**11**) *with Ethanol.*—9-Chloro-9-phenylxanthene (**11**) was prepared from 9-phenylxanthen-9-ol (**12a**) (1.25 g) and acetyl chloride (2 ml) in dry ether (15 ml) by the known method.[11] A solution of the chloroxanthene (**11**) in ethanol (40 ml) was refluxed for 30 min. The solvent was evaporated off to give 9-phenylxanthene (**10**) (0.95 g, 89%), which was identical with an authentic sample.[5a]

Reaction of the Chalcogenoxanthylium Salts (**1a**—**c**) *with Sodium Phenolate.*—(*a*) *In tetrahydrofuran or acetonitrile.* A suspension of sodium phenolate was prepared from sodium hydride (50% pure in mineral oil; 0.72 g, 15 mmol) and phenol (1.4 g, 15 mmol) in a solvent (50 ml). The chalcogenoxanthylium salt (**1**) (5 mmol) was added to the suspension of sodium phenolate. The mixture was stirred for 1 h at room temperature and then poured into water. The precipitate was filtered off, washed with water, and dried. The ether-soluble part was 9-phenoxy-9-phenylchalcogenoxanthene (**13a**—**c**) and the ether-insoluble part was *O*,4-bis(9-phenylchalcogenoxanthen-9-yl)phenol (**15a**—**c**).

(*b*) *In phenol.* Sodium hydride (50% pure in mineral oil) (0.72 g, 15 mmol) was added to phenol (30 ml) at 50 °C and the mixture was stirred until hydrogen gas evolution had ceased. The chalcogenoxanthylium salt (**1**) (5 mmol) was added to the solution of sodium phenolate. The reaction mixture was stirred for 1 h at 50 °C and then poured into water (300 ml). The white precipitate was filtered, washed with water, and dried. A similar work-up as described above gave 9-(*p*-hydroxyphenyl)-9-phenylchalcogenoxanthenes (**14a**—**c**).

Decomposition of O,4-*Bis*(9-*phenylxanthen*-9-*yl*)*phenol* (**15a**) *and the Seleno Derivative* (**15b**).—(*a*) Dry hydrogen chloride gas was bubbled through a solution of the bisxanthenylphenol (**15a**) (0.3 g) in dry benzene (50 ml) under reflux for 15 min. The mixture was refluxed for 5 h and the solvent was removed under reduced pressure. The residue was dissolved in ether, washed with aqueous $NaHCO_3$, and dried. The solvent was evaporated off and the residual solid was separated by preparative t.l.c. on silica gel using benzene. 9-Phenylxanthen-9-ol (**12a**) (0.13 g, 96%) and 9-(*p*-hydroxyphenyl)-9-phenylxanthene (**14a**) (0.13 g, 86.5%) were obtained. From the seleno derivative (**15b**), were obtained 9-phenylselenoxanthen-9-ol (**12c**) (76%), and 9-(*p*-hydroxyphenyl)-9-phenylselenoxanthene (**14c**) (83%).

(*b*) Silica gel (Wako gel C-200) (10 g) was added to a hot solution of the bisxanthenylphenol (**15a**) (1.0 g) in benzene (50 ml) and the mixture was warmed for 2 h. The solvent was removed and the residue was subjected to column chromatography on silica gel using benzene. 9-Phenylxanthene (0.37 g, 82%) and 9-(*p*-hydroxyphenyl)-9-phenylxanthene (0.40 g, 69%) were obtained.

9-(p-*Methoxyphenyl*)-9-*phenylchalcogenoxanthenes* (**16a**—**c**).—Sodium amide (0.53 g) was added to a solution of 9-(*p*-hydroxyphenyl)-9-phenylxanthene (**14a**) (0.40 g) in toluene (30 ml) and the mixture was refluxed for 3 h. Dimethyl sulphate (2 ml) was gradually added to the mixture which was then refluxed for 5 h. Aqueous sodium hydroxide was added to the cooled mixture and stirring was continued for 1 h at room temperature. The organic layer was separated and the aqueous layer was extracted with benzene. The extract was combined with the organic layer, dried (K_2CO_3), and evaporated. The residue was recrystallised from light petroleum–benzene to give 9-(p-*methoxyphenyl*)-9-*phenylxanthene* (**16a**) as colourless

prisms (0.36 g, 86.5%), m.p. 189 °C (Found: C, 85.7; H, 5.7. $C_{26}H_{20}O_2$ requires C, 85.7; H, 5.5%); δ 3.76 (3 H, s, OMe) and 6.58—7.57 (17 H, m, ArH). Similarly, 9-(*p*-hydroxyphenyl)-9-phenylthioxanthene (**14b**) and the seleno derivative (**14c**) yielded 9-(*p*-methoxyphenyl)-9-phenylthioxanthene (**16b**) (75.5%) and the selenoxanthene (**16c**) (66%), respectively, which were identical with the authentic samples (**16b**)[5b] and (**16c**).[5c]

Reaction of 9-Phenylchalcogenoxanthylium Salts (**1a**—**c**) *with Sodium Benzenethiolate.*—The chalcogenoxanthylium salt (**1**) (1.0 g, 2.3—2.7 mmol) was gradually added to a solution of sodium benzenethiolate [prepared from benzenethiol (0.9 g, 8.0 mmol) and sodium hydride (50% pure in mineral oil; 0.3 g, 8.0 mmol) in acetonitrile (10 ml)]. The mixture was stirred for 1 h at room temperature. Aqueous sodium chloride was added to the reaction and the resulting aqueous mixture was stirred for 30 min. The precipitate was filtered off and washed with light petroleum to remove benzenethiol. 9-Phenyl-9-(phenylthio)-xanthene (**17a**) (89%), -thioxanthene (**17b**) (92.5%), and -selenoxanthene (**17c**) (95%) were obtained and their physicochemical and spectral data are summarised in Tables 4 and 5, respectively.

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