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188. Addition of Xanthenyl and Thioxanthenyl Halides to Asymmetric Diarylethylenes and Their 2-Halogeno-Derivatives

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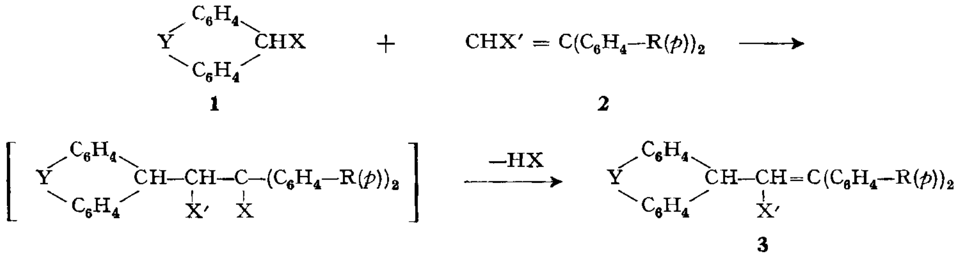
Summary. Xanthenyl and thioxanthenyl halides added readily to asymmetric diarylethylenes and their 2-halogeno-derivatives to give after dehydrohalogenation 1,1-diaryl-2-[xanthen(or thioxanthen)-9-yl]-ethylenes and 1,1-diaryl-2-halogeno-2-[xanthen(or thioxanthen)-9-yl]-ethylenes. The thioxanthenylethylenes were also obtained by another way.

Reactions of these ethylenes with bromine, chlorine or sulfuryl chloride were influenced by the halogen and the nature of the *p*-substituent.

Dehydrohalogenation of the 2-halogenoxanthenyl(or thioxanthenyl)ethylenes gave the corresponding 1,1-diaryl-2-[xanthen(or thioxanthen)-9-ylidene]-ethylenes.

We have reported [1] that xanthenyl chloride (**1**, Y = O, X = Cl) added readily to asymmetric diarylethylenes (**2a**, R = H, MeO, EtO, *i*-PrO, Me, Br or Cl) to give after dehydrohalogenation the corresponding 1,1-diaryl-2-(xanthen-9-yl)-ethylenes (**3a**, Y = O, R = H, MeO, EtO, *i*-PrO, Me, Br or Cl). Now we show that when oxygen in the xanthenyl residue was replaced by sulfur the addition reaction took place also. Thioxanthenyl bromide (**1**, Y = S, X = Br) or chloride (**1**, Y = S, X = Cl) added to asymmetric diarylethylenes (**2a**, R = H, MeO, EtO, *i*-PrO, Br or Cl) with formation of the corresponding 1,1-diaryl-2-(thioxanthen-9-yl)-ethylenes (**3a**, Y = S, R = H, MeO, EtO, *i*-PrO, Br or Cl). The structure of the latter (**3a**, Y = S) was confirmed by synthesis through the reaction between *p*-substituted phenylmagnesium bromide and methyl thioxanthenylacetate (see Exp. Part).

Xanthenyl and thioxanthenyl bromide or chloride (**1**, Y = O or S; X = Br or Cl) reacted with 1,1-bis-(*p*-alkoxyphenyl)-2-halogenoethylenes (**2b**, R = MeO, EtO or *i*-PrO) to yield the corresponding 1,1-bis-(*p*-alkoxyphenyl)-2-halogeno-2-[xanthen-(or thioxanthen)-9-yl]-ethylenes (**3b**, R = MeO, EtO or *i*-PrO)



2a, 3a X' = H **2b, 3b** X' = Br or Cl

As with xanthenylethylenes (**3a**, Y = O, R = H, MeO, EtO, *i*-PrO, Br or Cl) [1], the reaction of thioxanthenylethylenes (**3a**, Y = S, R = H, MeO, EtO, *i*-PrO, Br or Cl) with bromine was influenced by the nature of the *p*-substituent. In the presence of *p*-alkoxy groups (**3a**, Y = S, R = MeO, EtO or *i*-PrO), 1,1-bis-(*p*-alkoxyphenyl)-2-bromo-2-(thioxanthen-9-yl)-ethylenes (**3b**, Y = S, R = MeO, EtO or *i*-PrO) were obtained as the main product; small quantities of thioxanthenyl tribromide (**7**, Y = S), 1,1-diaryl-2-bromoethylenes (**2b**, X' = Br) and 1,1-diaryl-2,2-dibromoethylenes (**9**, X = Br) were also isolated. The compounds **7**, **2b** and **9** were the main products when the *p*-substituent was bromine, chlorine or hydrogen (**3a**, R = H, Br or Cl). In case of **3a**, R = H, 1,1-diphenyl-1,2,2-tribromoethane (**8**, R = H, X = Br) was also isolated.

With chlorine or sulfuryl chloride the *p*-alkoxyxanthenyl(or thioxanthenyl)-ethylenes (**3a**, Y = O or S; R = MeO, EtO or *i*-PrO) gave the corresponding 2-chloro-derivatives (**3b**, Y = O or S; X' = Cl; R = MeO, EtO or *i*-PrO) as the main product. When the substituent was Br, Cl or H (**3a**, Y = O or S; R = H, Br or Cl) 1,2-dichloro-(**4**, Y = O or S, X = Cl; R = H, Br or Cl) and the 2-chloro-(**3b**, Y = O or S; X' = Cl; R = H, Br or Cl) derivatives were obtained. Compounds **1** (Y = O or S, X = Cl) and **2b** (X' = Cl) were also isolated in the above reactions. The 1,2-dichloro-compounds (**4**, X = Cl, R = H, Br or Cl) were converted in boiling pyridine into the corresponding 2-chloro-derivatives (**3b**, X' = Cl; R = H, Br or Cl).

The structure of the 2-halogeno-derivatives (**3b**, X' = Br or Cl) was confirmed by ozonolysis which gave xanthenyl(or thioxanthenyl)-9-carboxylic acid and the corresponding benzophenones.

The allenes, 1,1-diaryl-2-[xanthen(or thioxanthen)-9-ylidene]-ethylenes (**5**, Y = O or S; R = H, MeO, EtO, *i*-PrO, Br or Cl) were prepared by dehydrohalogenation of the corresponding 2-bromo- or 2-chloro-derivatives (**3b**, Y = O or S; X' = Br or Cl; R = H, MeO, EtO, *i*-PrO, Br or Cl) with boiling methanolic potassium hydroxide.

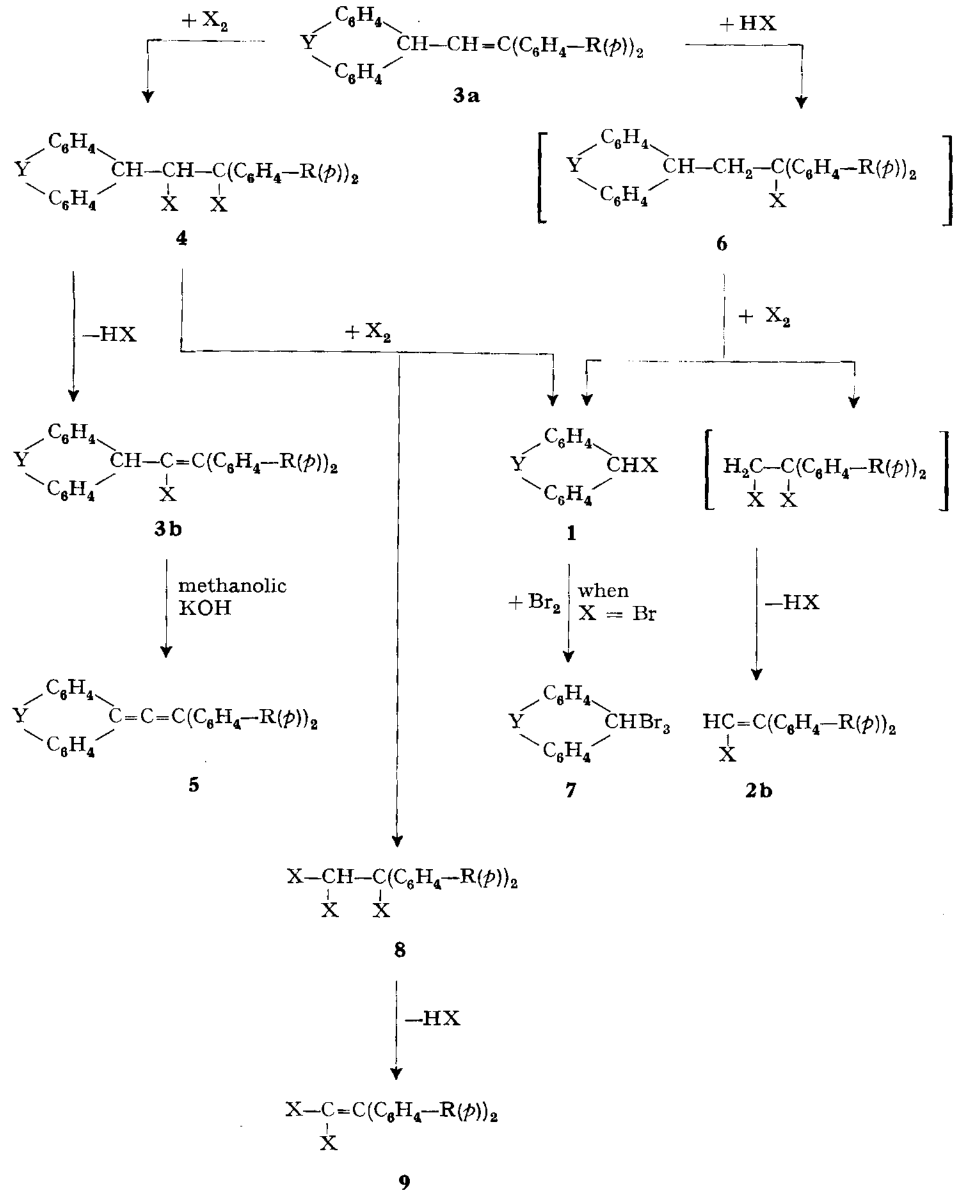
The NMR. spectra of these allenes **5** revealed the absence of both methine and vinyl protons, which were clearly discernible in the corresponding ethylenes **3a** (R = H, MeO or Cl): for Y = O, methine τ: 5.1; 5.0; 5.1; vinyl τ: 3.6; 3.8; 3.7; for Y = S methine τ: 5.2; 5.2; 5.3; vinyl τ: 3.2; 3.3; 3.2. In view of the difference of the electronic environments around the methine and vinyl protons doublets were shown by these protons. The vinyl proton disappeared in the NMR. spectra of the 2-chloro-derivatives (**3b**, Y = O or S; X = Cl; R = H, MeO or Cl) confirming the position of the halogen in this type of compounds as shown by ozonolysis.

The IR. absorption bands at 1070 cm^{-1} and 1950 cm^{-1} considered to be associated with the allenic structure [2–3] are either absent or weak in the allenes **5**.

In support of the direct cleavage of the inter-ring linkage at the 9-position in compounds **4** and **6** by halogens the following may be mentioned.

(1) 1,1-Diphenyl-1,2-dichloro-2-(xanthen-9-yl)-ethane (**4**, Y = O; X = Cl; R = H) reacted instantaneously with bromine to give xanthenyl tribromide (**7**, Y = O) and 1,1-diphenyl-2-bromo-2-chloroethylene.

(2) It has already been shown that xanthenylethylenes (**3a**, Y = O, R = H, MeO, EtO, *i*-PrO, Br or Cl) or their 2-bromo-derivatives (**3b**, Y = O, R = MeO, EtO or *i*-PrO) were not effected by hydrogen bromide alone [1]. However, in the presence of hydrogen bromide xanthenylethylenes (**3a**, Y = O; R = H, MeO, EtO,



i-PrO, Br or Cl) cleaved with bromine to give larger quantities of compounds **7** (Y = O) and **2b** (X′ = Br). We found also that in the presence of hydrogen bromide, the 2-bromo-derivatives **3b** (Y = O, X′ = Br) cleaved with bromine to give **7** and **9** (X = Br). Thioxanthenylethylenes (**3a**, Y = S) behaved similarly to give compounds **7** and **2b** (X and X′ = Br).

(3) *H. J. Shine* & *L. Hughes* [4] reported that thioxanthenyl tribromide (**7**, Y = S) was obtained in almost quantitative yield from the reaction of bromine with dithio-

xanthenyl. They explained the formation of the tribromide **7** to be due to an oxidative scission followed by further reaction with bromine. The electron density at the 9-xanthenyl [1] and 9-thioxanthenyl carbon bond in compounds **4** and **6** could well be of a similar nature.

The partial recovery of xanthenyl (or thioxanthenyl)-ethylenes (**3a**, Y = O or S; R = H, MeO, EtO, *i*-PrO, Br or Cl) when reacted with bromine was associated with a faster reaction between the cleaved product xanthenyl (or thioxanthenyl)bromide (**1**, Y = O or S, X = Br) and bromine. This was substantiated by reacting an equimolecular quantity of bromine with a mixture of xanthenyl bromide (**1**, Y = O, X = Br) and xanthenylethylene **3a** in solution in chloroform; xanthenyl tribromide (**7**, Y = O) was formed almost quantitatively whereas the ethylene **3a** was mainly recovered unchanged.

Experimental Part

IR. spectra were measured on *Beckman* IR. 4.

Thioxanthenyl bromide. Dry hydrogen bromide was bubbled through a cold solution of 2.0 g thioxanthenol (*cf.* [5–6]) in petrol (b.p. 60–80°, 100 ml) or chloroform (20 ml). The solvent was recovered under reduced pressure, and the residue was crystallised from dry petrol (b.p. 60–80°) to give thioxanthenyl bromide (2.2 g) as pale yellow crystals with m.p. 125° (dec.).

$C_{13}H_9BrS$ Calc. Br 28.9 S 11.6% Found Br 28.5 S 11.3%

Thioxanthenyl tribromide. Bromine (1.6 g = 0.01 mol) was added to a solution of thioxanthenyl bromide (2.77 g = 0.01 mol) in chloroform or carbon tetrachloride (20 ml). Thioxanthenyl tribromide (4.0 g) precipitated immediately as scarlet-red crystals which were filtered off and washed with dry petrol: m.p. 185°.

$C_{13}H_9Br_3S$ Calc. Br 54.9 S 7.3% Found Br 54.4 S 7.8%

*1,1-Bis-(*p*-isopropoxyphenyl)-2-chloroethylene.* Sulfuryl chloride (1.35 g = 0.01 mol) in carbon tetrachloride (10 ml) was added to a solution of 1,1-bis-(*p*-isopropoxyphenyl)-ethylene (2.96 g = 0.01 mol) in the same solvent. The mixture was heated on the water-bath for 30 min. The solvent was recovered and the residue was crystallised from petrol (b.p. 40–60°) to give 1,1-bis-(*p*-isopropoxyphenyl)-2-chloroethylene (3.0 g), m.p. 55°.

$C_{20}H_{23}ClO_2$ Calc. C 72.6 H 6.9 Cl 10.7% Found C 72.1 H 6.5 Cl 10.6%

Addition of Thioxanthenyl bromide or chloride to asymmetric diarylethylenes (Table 1). This is exemplified as follows: A solution of thioxanthenyl bromide (2.77 g = 0.01 mol) or chloride (*cf.* [7]) (2.32 g = 0.01 mol) and asymmetric diarylethylene (0.01 mol) in dry ether (50 ml) was heated to boiling for 2 h. and then left overnight. The solvent was recovered and the residue was digested for 15 min. with ethanolic potassium hydroxide (1 g in 30 ml). The mixture was cooled, diluted with water and extracted with ether. The ethereal layer was washed with water till free from alkali, and dried (Na_2SO_4). Ether was recovered and the residue was crystallised from 95% ethanol to give 1,1-bis-(*p*-substituted phenyl)-2-(thioxanthen-9-yl)-ethylenes as colourless crystals (yield with thioxanthenyl bromide was *ca.* 75%, and with the chloride *ca.* 60%).

Compounds **3a** (Y = O) [1] were also obtained in better yields (*ca.* 75%) from the reaction of **1** (Y = O, X = Br) (0.01 mol) with **2a** (0.01 mol).

*Addition of xanthenyl and thioxanthenyl halides to 1,1-bis-(*p*-alkoxyphenyl)-2-halogenoethylenes* (Table 2). This is exemplified by the following: A solution of xanthenyl bromide (*cf.* [8]) (2.61 g = 0.01 mol) or thioxanthenyl bromide (2.77 g = 0.01 mol) and 1,1-bis-(*p*-alkoxyphenyl)-2-bromo (or chloro)ethylene (0.01 mol) in dry ether or chloroform (50 ml) was left overnight at room temperature. The solvent was recovered and the residue was crystallised from 95% ethanol to give the corresponding 1,1-bis-(*p*-alkoxyphenyl)-2-bromo(or chloro)-2-[xanthen(or thioxanthen)-9-yl]-ethylene in *ca.* 60% yield. The 2-bromo-(~50%) and 2-chloro-(~40%) derivatives (Y = O or S) were also obtained from the reaction of xanthenyl (*cf.* [9]) (or thioxanthenyl) chloride **1** (Y = O or S, X = Cl) (0.01 mol) with the corresponding 2-bromo(or chloro) ethylene **2b** (X′ = Br or Cl) (0.01 mol).

Table 1. *1,1-Diaryl-2-(thioxanthen-9-yl)-ethylenes* **3a** (*Y* = *S*)

R	M.p.	Analytical Data	Calc.	Found
H	134°	$C_{27}H_{20}S$	C 86.2 H 5.3 S 8.5%	C 86.2 H 4.9 S 8.9%
MeO	135°	$C_{29}H_{24}O_2S$	C 79.8 H 5.5 S 7.3%	C 80.2 H 5.5 S 7.4%
EtO	156°	$C_{31}H_{28}O_2S$	C 80.2 H 6.0 S 6.9%	C 79.7 H 5.8 S 7.4%
i-PrO	139°	$C_{33}H_{32}O_2S$	C 80.5 H 6.5 S 6.5%	C 80.2 H 6.4 S 6.8%
Br	135°	$C_{27}H_{18}Br_2S$	C 60.7 H 3.4 Br 30.0 S 6.0%	C 60.3 H 3.7 Br 29.8 S 5.9%
Cl	126°	$C_{27}H_{18}Cl_2S$	C 72.8 H 4.0 Cl 15.9 S 7.2%	C 72.4 H 3.8 Cl 15.7 S 7.2%

Table 2. *1,1-Bis-*(p*-alkoxyphenyl)-2-bromo(or chloro)-2-[xanthen(or thioxanthen)-9-yl]-ethylenes* **3b**

R	X	Y	M.p.	Analytical Data	Calc.	Found
MeO	Br	O	141°	$C_{29}H_{23}BrO_3$	Br 16.1%	Br 16.1%
EtO	Br	O	152°	$C_{31}H_{27}BrO_3$	Br 15.2%	Br 14.9%
i-PrO	Br	O	130°	$C_{33}H_{31}BrO_3$	Br 14.4%	Br 14.8%
MeO	Cl	O	141°	$C_{29}H_{23}ClO_3$	Cl 7.8%	Cl 8.0%
EtO	Cl	O	138°	$C_{31}H_{27}ClO_3$	Cl 7.4%	Cl 7.4%
i-PrO	Cl	O	142°	$C_{33}H_{31}ClO_3$	Cl 7.0%	Cl 6.9%
MeO	Br	S	152°	$C_{29}H_{23}BrO_2S$	Br 15.5 S 6.2%	Br 15.3 S 6.4%
EtO	Br	S	126°	$C_{31}H_{27}BrO_2S$	Br 14.7 S 5.9%	Br 15.0 S 5.4%
i-PrO	Br	S	145°	$C_{33}H_{31}BrO_2S$	Br 14.0 S 5.6%	Br 13.9 S 5.6%
MeO	Cl	S	142°	$C_{29}H_{23}ClO_2S$	Cl 7.5 S 6.8%	Cl 7.8 S 6.9%
EtO	Cl	S	136°	$C_{31}H_{27}ClO_2S$	Cl 7.1 S 6.4%	Cl 7.0 S 6.4%
i-PrO	Cl	S	180°	$C_{33}H_{31}ClO_2S$	Cl 6.7 S 6.1%	Cl 7.0 S 6.2%

Synthesis of thioxanthenylethylenes. This is exemplified by the preparation of 1,1-diphenyl-2-(thioxanthen-9-yl)-ethylene: A solution of methyl thioxanthenylacetate (*cf.* [10]) (2.7 g = 0.01 mol) in dry ether (15 ml) was added at room temperature within 30 min. with constant stirring to phenylmagnesium bromide (Mg: 1.2 g = 0.05 mol; bromobenzene: 7.85 g = 0.05 mol; dry ether: 15 ml). The whole mixture was subsequently heated on the water bath for 30 min. and left overnight. The mixture was decomposed with aqueous ammonium chloride and the ethereal layer washed with water, and dried (Na_2SO_4). Ether was recovered and the residue was crystallised from 95% ethanol to give colourless crystals of 1,1-diphenyl-2-(thioxanthen-9-yl)-ethylene with m.p. and mixed m.p. 134° (2.2 g). Similarly were prepared (yield ~65%) and crystallised from 95% ethanol as colourless crystals; 1,1-bis-(*p*-methoxyphenyl)-2-(thioxanthen-9-yl)-ethylene, m.p. and mixed m.p. 135°, and 1,1-bis-(*p*-chlorophenyl)-2-(thioxanthen-9-yl)-ethylene, m.p. and mixed m.p. 126°.

Reaction of Bromine. (a) *With 1,1-bis-*(p*-alkoxyphenyl)-2-(thioxanthen-9-yl)-ethylenes.* (i) Bromine (0.8 g = 0.005 mol) in chloroform (5 ml) was added to a solution of 1,1-bis-(*p*-methoxyphenyl)-2-(thioxanthen-9-yl)-ethylene (2.18 g = 0.005 mol) in the same solvent (20 ml). A scarlet-red precipitate of thioxanthenyl tribromide, m.p. and mixed m.p. 185°, separated instantaneously; petrol was added to complete the precipitation (0.2 g). The combined solvents were removed at room temperature and the residue was crystallised from petrol (b.p. 60–80°) to give 1,1-bis-(*p*-methoxyphenyl)-2-bromo-2-(thioxanthen-9-yl)-ethylene (2.0 g), m.p. and mixed m.p. 152°, and unchanged 1,1-bis-(*p*-methoxyphenyl)-2-(thioxanthen-9-yl)-ethylene (0.1 g), m.p. and mixed m.p. 135°. The mother liquor was concentrated and the semi-solid product obtained was crystallised from 95% ethanol to give 1,1-bis-(*p*-methoxyphenyl)-2-bromoethylene (0.2 g), m.p. and mixed m.p. (*cf.* [11]) 84°, and 1,1-bis-(*p*-methoxyphenyl)-2,2-dibromoethylene (0.02 g), m.p. and mixed m.p. (*cf.* [12]) 91°. (ii) The repetition of (i) using 1,1-bis-(*p*-ethoxyphenyl)-2-(thioxanthen-9-yl)-ethylene (2.32 g = 0.005 mol) gave thioxanthenyl tribromide (0.2 g), 1,1-bis-(*p*-ethoxyphenyl)-2-bromo-2-(thioxanthen-9-yl)-ethylene (2.1 g), m.p. and mixed m.p. 126°, 1,1-bis-(*p*-ethoxyphenyl)-2-bromoethylene (0.2 g), m.p. and mixed m.p. (*cf.* [13]) 64°, 1,1-bis-(*p*-ethoxyphenyl)-2,2-dibromoethylene, m.p. and mixed m.p. (*cf.* [12]) 118° and unchanged 1,1-bis-(*p*-ethoxyphenyl)-2-(thioxanthen-9-yl)-ethylene (0.1 g), m.p. and mixed m.p. 156°. (iii) The same reaction using 1,1-bis-(*p*-isopropoxyphenyl)-2-(thioxanthen-9-yl)-ethylene (2.46 g = 0.005 mol) gave thioxanthenyl tribromide (0.2 g), 1,1-bis-(*p*-isopropoxyphenyl)-2-bromo-2-(thioxanthen-9-yl)-ethylene (2.3 g), m.p. and mixed m.p. 145°, 1,1-bis-(*p*-isopropoxyphenyl)-2-bromoethylene (0.2 g), m.p. and mixed m.p. (*cf.* [14]) 46° and unchanged 1,1-bis-(*p*-isopropoxyphenyl)-2-(thioxanthen-9-yl)-ethylene (0.1 g), m.p. and mixed m.p. 139°. (iv) When the above experiments (i, ii, iii) were repeated in the same solvent saturated with hydrogen bromide, the following compounds were obtained: thioxanthenyl tribromide (1.1 g), 1,1,4,4-tetrakis-(*p*-alkoxyphenyl)buta-1,3-diene (0.1 g), *p*-methoxy, m.p. and mixed m.p. (*cf.* [15]) 204°, *p*-ethoxy, m.p. and mixed m.p. (*cf.* [13]) 202°, *p*-isopropoxy, m.p. and mixed m.p. (*cf.* [16]) 187°; 1,1-bis-(*p*-alkoxyphenyl)-2-bromo-2-(thioxanthen-9-yl)-ethylene (0.1 g) and 1,1-bis-(*p*-alkoxyphenyl)-2-bromoethylene (0.7 g).

(b) *With 1,1-diphenyl-2-(thioxanthen-9-yl)-ethylene.* Bromine (1.6 g = 0.01 mol) in chloroform (5 ml) was added to a solution of 1,1-diphenyl-2-(thioxanthen-9-yl)-ethylene (3.75 g = 0.01 mol) in the same solvent (20 ml). Petrol (b.p. 60–80°, 50 ml) was added and thioxanthenyl tribromide (2.1 g) was filtered off. The combined solvents were removed at room temperature and the residue was crystallised from petrol (b.p. 60–80°) from which unchanged 1,1-diphenyl-2-(thioxanthen-9-yl)-ethylene (1.8 g), m.p. and mixed m.p. 134°, and 1,1-diphenyl-1,2,2-tribromoethane (0.12 g), m.p. and mixed m.p. (*cf.* [17]) 89° were obtained. The mother liquor was concentrated and the oily product thus obtained was steam-distilled. The steamable portion was extracted with ether. Ether was recovered and the residue was crystallised from 95% ethanol to give 1,1-diphenyl-2-bromoethylene (0.7 g), m.p. and mixed m.p. (*cf.* [18]) 42°. The non-steamable portion was extracted with ether. The solvent was recovered and the residue was crystallised from 95% ethanol from which 1,1-diphenyl-2,2-dibromoethylene (0.2 g), m.p. and mixed m.p. (*cf.* [17]) 83° was isolated.

(c) *With 1,1-bis-*(p*-halogenophenyl)-2-(thioxanthen-9-yl)-ethylenes.* (i) Repetition of experiment (b) with 1,1-bis-(*p*-bromophenyl)-2-(thioxanthen-9-yl)-ethylene (2.67 g = 0.005 mol) gave thioxanthenyl tribromide (1.0 g), unchanged 1,1-bis-(*p*-bromophenyl)-2-(thioxanthen-9-yl)-ethylene (1.2 g), m.p. and mixed m.p. 135°, 1,1-bis-(*p*-bromophenyl)-2-bromoethylene (0.6 g), m.p. and mixed m.p. (*cf.* [19]) 104°, and 1,1-bis-(*p*-bromophenyl)-2,2-dibromoethylene (0.2 g), m.p. and mixed m.p. (*cf.* [20]) 122°. (ii) Repetition of (i) using 1,1-bis-(*p*-chlorophenyl)-2-(thioxanthen-9-yl)-ethylene gave thioxanthenyl tribromide (1.1 g), unchanged 1,1-bis-(*p*-chlorophenyl)-2-(thioxanthen-9-yl)-ethylene (1.0 g), m.p. and mixed m.p. 126°, 1,1-bis-(*p*-chlorophenyl)-2-bromoethylene (0.5 g), m.p. and mixed m.p. (*cf.* [19]) 76°, and 1,1-bis-(*p*-chlorophenyl)-2,2-dibromoethylene (0.2 g), m.p. and mixed m.p. (*cf.* [20]) 104°.

(d) *With 1,1-diphenyl-1,2-dichloro-2-(xanthen-9-yl)-ethane.* Bromine (0.32 g = 0.002 mol) in chloroform (2 ml) was added to a solution of the ethane (0.86 g = 0.002 mol) in the same solvent. Petrol was added, xanthenyl tribromide (0.4 g), m.p. and mixed m.p. (*cf.* [8]) 164°, was filtered off. The combined solvents were recovered and the residue was crystallised from dry petrol to give unchanged ethane (0.4 g), m.p. and mixed m.p. 136° and 1,1-diphenyl-2-bromo-2-chloroethylene (0.2 g), m.p. and mixed m.p. with an authentic sample 76° [prepared by the reaction of an equimolecular quantity of bromine (1.6 g) with 1,1-diphenyl-2-chloroethylene (2.14 g) in benzene (20 ml)]. $C_{14}H_{10}BrCl$ Calc. Br 27.3 Cl 12.0% Found Br 27.3 Cl 11.8%

(e) *With a mixture of xanthenyl bromide and 1,1-bis-*(p*-substituted phenyl)-2-(xanthen-9-yl)-ethylene.* (i) Bromine (0.16 g = 0.001 mol) in chloroform (5 ml) was added to a mixture of xanthenyl bromide (0.26 g = 0.001 mol) and 1,1-bis-(*p*-isopropoxyphenyl)-2-(xanthen-9-yl)-ethylene (0.476 g = 0.001 mol) in solution in chloroform (20 ml). Petrol was added to the mixture and the yellow precipitate was filtered off to give xanthenyl tribromide, (0.4 g), m.p. and mixed m.p. (*cf.* [8]) 164°. The combined solvents were recovered and the residue was crystallised from 95% ethanol to give unchanged 1,1-bis-(*p*-isopropoxyphenyl)-2-(xanthen-9-yl)-ethylene (0.45 g), m.p. and mixed m.p. (*cf.* [1]) 169°. (ii) Repetition of experiment (i) with 1,1-bis-(*p*-chlorophenyl)-2-(xanthen-9-yl)-ethylene (0.429 g = 0.001 mol) gave xanthenyl tribromide (0.4 g), m.p. and mixed m.p. (*cf.* [8]) 164°, and unchanged alkene (0.42 g), m.p. and mixed m.p. (*cf.* [1]) 157°.

Reactions of Chlorine. – (a) *With 1,1-bis-*(p*-alkoxyphenyl)-2-(xanthen-9-yl)-ethylenes.* (i) Chlorine (0.355 g = 0.005 mol) in carbon tetrachloride (5 ml) was added to a solution of 1,1-bis-(*p*-

methoxyphenyl)-2-(xanthen-9-yl)-ethylene (2.1 g = 0.005 mol) in the same solvent (20 ml). The mixture was left at room temperature overnight. The solvent was recovered and the residue was crystallised from petrol (b.p. 60–80°) to give 1,1-bis-(*p*-methoxyphenyl)-2-chloro-2-(xanthen-9-yl)-ethylene (0.2 g), m.p. and mixed m.p. 141°, xanthenyl chloride (trace), m.p. and mixed m.p. (*cf.* [9]) 74°, and unchanged alkene (1.25 g), m.p. and mixed m.p. (*cf.* [1]) 94°. The mother liquor was concentrated and the oily residue was crystallised from 95% ethanol to give xanthone (trace), m.p. and mixed m.p. (*cf.* [21]) 174°, xanthene (0.05 g), m.p. and mixed m.p. (*cf.* [22]) 100° [the formation of xanthene and xanthone may be attributed to the reactivity of xanthenyl chloride when the products were treated with hydroxylic solvents (*cf.* [9])], and 1,1-bis-(*p*-methoxyphenyl)-2-chloroethylene (0.1 g), m.p. and mixed m.p. (*cf.* [19]) 76°. (ii) The repetition of experiment (i) using 1,1-bis-(*p*-ethoxyphenyl)-2-(xanthen-9-yl)-ethylene (2.24 g = 0.005 mol) gave 1,1-bis-(*p*-ethoxyphenyl)-2-chloro-2-(xanthen-9-yl)-ethylene (0.2 g), m.p. and mixed m.p. 138°, xanthenyl chloride (trace), xanthone (trace), xanthene (0.05 g), 1,1-bis-(*p*-ethoxyphenyl)-2-chloroethylene (0.1 g), m.p. and mixed m.p. (*cf.* [19]) 76° and unchanged alkene (1.6 g), m.p. and mixed m.p. (*cf.* [1]) 115°. (iii) The products of the reaction with 1,1-bis-(*p*-isopropoxyphenyl)-2-(xanthen-9-yl)-ethylene (2.38 g = 0.005 mol) were: 1,1-bis-(*p*-isopropoxaphenyl)-2-chloro-2-(xanthen-9-yl)-ethylene, m.p. and mixed m.p. 141° (0.2 g), xanthenyl chloride (trace), xanthone (trace), xanthene (0.05 g), 1,1-bis-(*p*-isopropoxyphenyl)-2-chloroethylene, m.p. 55°, and unchanged alkene (1.7 g) m.p. and mixed m.p. (*cf.* [1]) 169°.

(b) *With 1,1-diphenyl-2-(xanthen-9-yl)-ethylene.* When experiment (a, i) was repeated with 1,1-diphenyl-2-(xanthen-9-yl)-ethylene the following products were obtained: *1,1-diphenyl-1,2-dichloro-2-(xanthen-9-yl)-ethane* (0.2 g), m.p. 136° ($C_{27}H_{20}Cl_2O$ Calc. Cl 16.5% Found Cl 16.4%), *1,1-diphenyl-2-chloro-2-(xanthen-9-yl)-ethylene* (0.05 g), m.p. 185° ($C_{27}H_{19}ClO$ Calc. Cl 9.0% Found Cl 9.2%), xanthenyl chloride (trace), xanthone (trace), xanthene (0.05 g), 1,1-diphenyl-2-chloroethylene (0.05 g), m.p. and mixed m.p. (*cf.* [23]) 42°, and unchanged alkene (1.25 g), m.p. and mixed m.p. (*cf.* [1]) 164°.

(c) *With 1,1-bis-*(p*-halogenophenyl)-2-(xanthen-9-yl)-ethylene.* Repetition of experiment (a, i) with 1,1-bis-(*p*-bromophenyl)-2-(xanthen-9-yl)-ethylene gave *1,1-bis-*(p*-bromophenyl)-1,2-dichloro-2-(xanthen-9-yl)-ethane* (0.3 g), m.p. 166° ($C_{27}H_{18}Br_2Cl_2O$ Calc. Br 27.2 Cl 12.1% Found Br 27.2 Cl 12.0%), *1,1-bis-*(p*-bromophenyl)-2-chloro-2-(xanthen-9-yl)-ethylene* (0.05 g), m.p. 200° ($C_{27}H_{17}Br_2ClO$ Calc. Br 29.0 Cl 6.4% Found Br 29.2 Cl 6.5%), xanthenyl chloride (trace), xanthone (trace), xanthene (0.05 g), 1,1-bis-(*p*-bromophenyl)-2-chloroethylene (0.05 g), and mixed m.p. (*cf.* [24]) 107°.

Reactions of sulfuryl chloride (Table 3). This is exemplified by the reaction with 1,1-diphenyl-2-(xanthen-9-yl)-ethylene. Sulfuryl chloride (0.67 g = 0.005 mol) in carbon tetrachloride (20 ml) was added to a solution of 1,1-diphenyl-2-(xanthen-9-yl)-ethylene (1.8 g = 0.005 mol) in the same solvent (20 ml). The mixture was heated on the boiling waterbath for 30 min. The solvent was recovered under dry nitrogen and the residue was crystallised from petrol (b.p. 60–80°) from which 1,1-diphenyl-1,2-dichloro-2-(xanthen-9-yl)-ethane (1.3 g) separated as colourless crystals with m.p. and mixed m.p. 136°. Concentration of the filtrate and fractionation from petrol gave 1,1-diphenyl-2-chloro-2-(xanthen-9-yl)-ethylene (0.15 g), m.p. and mixed m.p. 185°, xanthenyl chloride (0.05 g) and unchanged ethylene (0.1 g), m.p. and mixed m.p. (*cf.* [1]) 164°. Petrol of the final mother liquor was recovered and the residue was steam-distilled. The steamable portion was extracted with ether. The latter was removed and the residue when crystallised from 95% ethanol gave xanthone (0.05 g) and xanthene (0.1 g). The non-steamable portion was extracted with ether, which was recovered, and the residue was crystallised from 95% ethanol from which 1,1-diphenyl-2-chloroethylene separated as colourless crystals (0.15 g), m.p. and mixed m.p. (*cf.* [23]) 42°.

1,1-Bis-[phenyl(or p*-halogenophenyl)]-2-chloro-2-[xanthen(or thioxanthen)-9-yl]-ethylenes.* A solution of 1,1-bis-[phenyl-(or *p*-halogenophenyl)]-1,2-dichloro-2-[xanthen(or thioxanthen)-9-yl]-ethane (0.1 g) in pyridine (20 ml) was heated to boiling for 30 min., cooled, diluted with water and the precipitate filtered off. The precipitate was washed thoroughly with water and then crystallised from 96% ethanol to give the corresponding 1,1-bis-[phenyl(or *p*-halogenophenyl)]-2-chloro-2-[xanthen(or thioxanthen)-9-yl]-ethylene (~90%) as colourless crystals; thus were obtained: 1,1-diphenyl-2-chloro-2-(xanthen-9-yl)-ethylene, m.p. and mixed m.p. 185°, 1,1-bis-(*p*-bromophenyl)-2-chloro-2-(xanthen-9-yl)-ethylene, m.p. and mixed m.p. 200°; 1,1-bis-(*p*-chlorophenyl)-

Table 3. *Reactions of xanthenyl(or thioxanthenyl)-ethylenes* (**3a**, 0.005 mol) *and sulfuryl chloride* (0.005 mol)

Reactant			Resultants					
3a (X = H)			**4** (X = Cl)		**3b** (X = Cl)		**2b** (X = Cl)	**1** (X = Cl)
Y	R	g	g	m.p. (°C)	g	m.p. (°C)	g	g
O	H	1.80	1.3	136	0.15	185	0.15	0.05
O	MeO	2.10	–	–	2.00	142	0.05	0.03
O	EtO	2.24	–	–	2.00	138	0.05	0.03
O	*i*-PrO	2.38		–	2.30	141	0.03	0.02
O	Br	2.58	1.6	166	0.20	200	0.20	0.05
O	Cl	2.145	1.4	163[a]	0.15	205[e]	0.15	0.05
S	H	1.88	1.3	150[b]	0.15	165[f]	0.15	0.05
S	MeO	2.18	–	–	2.00	153	0.04	0.03
S	EtO	2.32	–	–	2.10	130	0.05	0.03
S	*i*-PrO	2.46	–	–	2.40	185	0.03	0.02
S	Br	2.67	1.7	155[c]	0.15	218[g]	0.15	0.05
S	Cl	2.225	1.4	151[d]	0.15	210[h]	0.15	0.05

Xanthone (or thioxanthone) (0.03–0.05 g), xanthene (or thioxanthene) (0.05–0.10 g) and unchanged xanthenyl(or thioxanthenyl)-ethylenes (0.1 g) were also obtained.

[a] $C_{27}H_{18}Cl_4O$ Calc. Cl 28.4% Found Cl 28.2%.

[b] $C_{27}H_{18}Cl_2S$ Calc. Cl. 15.9 S 7.2% Found Cl 15.7 S 7.1%.

[c] $C_{27}H_{18}Br_2Cl_2S$ Calc. Br 26.4 Cl 11.7 S 5.3% Found Br 26.6 Cl 11.5 S 5.4%.

[d] $C_{27}H_{18}Cl_4S$ Calc. Cl 27.5 S 6.2% Found Cl 27.1 S 6.6%.

[e] $C_{27}H_{17}Cl_3O$ Calc. Cl 23.0% Found Cl 22.5%.

[f] $C_{27}H_{17}ClS$ Calc. 8.6 S 7.8% Found Cl 9.0 S 7.3%.

[g] $C_{27}H_{17}Br_2ClS$ Calc. Br 28.1 Cl 6.2 S 5.6% Found Br 27.7 Cl 5.8 S 5.8%.

[h] $C_{27}H_{17}Cl_3S$ Calc. Cl 22.2 S 6.7% Found Cl 22.2 S 6.3%.

2-chloro-2-(xanthen-9-yl)-ethylene, m.p. and mixed m.p. 205°; 1,1-diphenyl-2-chloro-2-(thioxanthen-9-yl)-ethylene, m.p. and mixed m.p. 165°; 1,1-bis-(*p*-bromophenyl)-2-chloro-2-(thioxanthen-9-yl)-ethylene, m.p. 218°; and 1,1-bis-(*p*-chlorophenyl)-2-chloro-2-(thioxanthen-9-yl)-ethylene, m.p. and mixed m.p. 210°.

Ozonolysis (cf. [1]) *of 1,1-bis-*(p-*substituted phenyl*)*-2-bromo*(*or chloro*)*-2-*[*xanthen*(*or thioxanthen*)*-9-yl*]*-ethylenes.* Ozonolysis gave: xanthen-9-carboxylic acid, m.p. and mixed m.p. (*cf.* [25]) 220° or thioxanthen-9-carboxylic acid, m.p. and mixed m.p. (*cf.* [26]) 228° and the corresponding *p*-substituted benzophenones; benzophenone (identified as its 2,4-dinitrophenylhydrazone, m.p. and mixed m.p. 238°); 4,4′-dimethoxybenzophenone, m.p. and mixed m.p. (*cf.* [27]) 142°; 4,4′-diethoxybenzophenone, m.p. and mixed m.p. (*cf.* [27]) 135°; 4,4′-di-isopropoxybenzophenone, m.p. and mixed m.p. (*cf.* [27]) 74°; 4,4′-dibromobenzophenone, m.p. and mixed m.p. (*cf.* [28]) 172°; 4,4′-dichlorobenzophenone, m.p. and mixed m.p. (*cf.* [29]) 145°.

1,1-Bis-(p-*substituted phenyl*)*-2-*[*xanthen*(*or thioxanthen*)*-9-ylidene*]*-ethylenes.* These were obtained (~75%) by heating to boiling a mixture of 1,1-bis-(*p*-substituted phenyl)-2-bromo(or chloro-) 2-[xanthen(or thioxanthen)-9-yl]-ethylenes (1.0 g) and methanolic potassium hydroxide (2.0 g in 50 ml) for 5 h. The mixture was cooled, diluted with water (50 ml) and extracted with ether. The ethereal layer was washed with water till free from alkali. Ether was recovered and the residue was crystallised from 95% ethanol from which separated as colourless crystals: 1,1-diphenyl-2-(xanthen-9-ylidene)-ethylene, m.p. and mixed m.p. (*cf.* [17]) 205°; 1,1-bis-(*p*-methoxyphenyl)-2-(xanthen-9-ethylene, m.p. and mixed m.p. (*cf.* [1]) 125°; 1,1-bis-(*p*-ethoxyphenyl)-2-(xanthen-9-ylidene)-ethylene, m.p. and mixed m.p. (*cf.* [1]) 125°; 1,1-bis-(*p*-isopropoxyphenyl)-2-(xanthen-9-ylidene)-ethylene, m.p. and mixed m.p. (*cf.* [1]) 147°; *1,1-bis-*(p-*bromophenyl*)*-2-*(*xanthen-9-*

ylidene)-ethylene, m.p. 195° ($C_{27}H_{16}Br_2O$ Calc. C 62.8 H 3.1 Br 31.0% Found C 62.6 H 3.5 Br 30.9%) *1,1-bis-*(p-*chlorophenyl)-2-(xanthen-9-ylidene)-ethylene*, m.p. 182° ($C_{27}H_{16}Cl_2O$ Calc. C 75.9 H 3.7 Cl 16.6% Found C 75.4 H 3.9 Cl 16.4%).

Table 4. *1,1-bis-*(p-*substituted phenyl)-2-(thioxanthen-9-ylidene)-ethylenes* **5** (Y = S)

R	m.p.	Analytical Data	Calc.	Found
H	196°	$C_{27}H_{18}S$	C 86.6 H 4.8 S 8.6%	C 86.2 H 4.9 S 8.6%
MeO	120°	$C_{29}H_{22}O_2S$	C 80.2 H 5.1 S 7.4%	C 80.0 H 5.2 S 7.3%
EtO	109°	$C_{31}H_{26}O_2S$	C 80.5 H 5.6 S 6.9%	C 80.3 H 5.6 S 7.1%
i-PrO	123°	$C_{33}H_{30}O_2S$	C 80.8 H 6.1 S 6.5%	C 80.3 H 5.7 S 6.4%
Br	146°	$C_{27}H_{16}Br_2S$	C 60.9 H 3.0 Br 30.1 S 6.0%	C 60.9 H 3.0 Br 30.0 S 6.5%
Cl	169°	$C_{27}H_{16}Cl_2S$	C 73.1 H 3.6 Cl 16.0 S 7.2%	C 72.5 H 3.6 Cl 15.7 S 7.2%

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