Studies on Xanthenyl and Thioxanthenyl Derivatives. Reactions of Xanthenyl and Thioxanthenyl Halides with Substituted-Ethylenes

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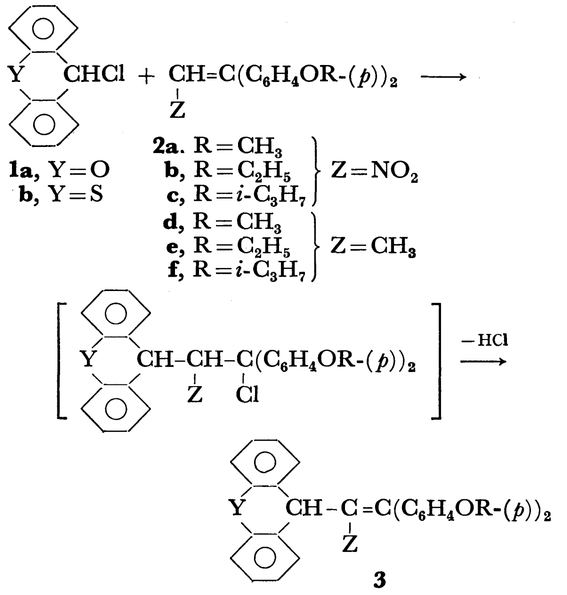
Xanthenyl and thioxanthenyl chlorides (**1**) were added to 1,1-bis-(*p*-alkoxyphenyl)-2-substituted-ethylenes (**2**) to give 1,1-bis-(*p*-alkoxyphenyl)-2-substituted-2-[xanthen(or thioxanthen)-9-yl]ethylenes (**3**). The 2-nitro-derivatives (**3**) were converted in boiling methanolic potassium hydroxide into the allenes, 1,1-bis-(*p*-alkoxyphenyl)-2-[xanthen(or thioxanthen)-9-ylidene]ethylenes (**4**). The 2-methyl(or chloro)-derivatives (**3**) reacted with bromine in the presence of hydrogen bromide, to yield xanthylium or thioxanthylium tribromide (**5**) and the corresponding 2,2-disubstituted-ethylene (**6**). The tribromides (**5**) reacted with the ethylene (**2**, Z=H) to give, after spontaneous dehydrobromination, the corresponding 2-bromo-derivatives (**3**, Z=Br).

In a preceding publication,[1] it has been shown that xanthenyl and thioxanthenyl chlorides (**1a**,**b**) were added to 1,1-bis-(*p*-alkoxyphenyl)ethyleness (**2**, Z=H) and their 2-bromo(or chloro)-derivatives (**2**, Z=Br or Cl) to give the corresponding 1,1-bis-(*p*-alkoxyphenyl)-2-[xanthen (or thioxanthen)-9-yl]ethylenes (**3**, Z=H) and the orresponding 1,1-bis(*p*-alkoxyphenyl)-2-bromo(or chloro)-2-[xanthen(or thioxanthen)-9-yl]ethylenes (**3**, Z=Br or Cl), respectively. We now show that each of xanthenyl and thioxanthenyl chlorides (**1a**, **b**) was added to 1,1-bis-(*p*-alkoxyphenyl)-2-nitro(and methyl)ethylenes (**2a**—**f**) to give, after spontaneous dehydrochlorination, the corresponding 1,1-bis-(*p*-alkoxyphenyl)-2-nitro-(and methyl)-2-[xanthen(or thioxanthen)-9-yl]ethylenes (**3a**—**l**). The 1,1-bis-(*p*-alkoxyphenyl)-2-nitroethylenes (**2a**—**c**) are prepared by treating the corresponding 1,1-bis-(*p*-alkoxyphenyl)-2-bromoethylenes (**2**, Z=Br) with silver nitrite.



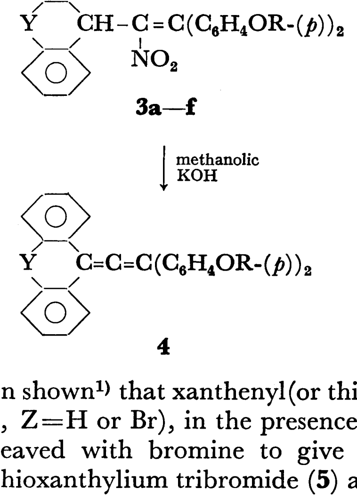
1a, Y=O
b, Y=S

2a. R=CH_3, **b**, R=C_2H_5, **c**, R=i-C_3H_7 } Z=NO_2
d, R=CH_3, **e**, R=C_2H_5, **f**, R=i-C_3H_7 } Z=CH_3

3

3a, R=CH_3, **b**, R=C_2H_5, **c**, R=i-C_3H_7 } Y=O, Z=NO_2
d, R=CH_3, **e**, R=C_2H_5, **f**, R=i-C_3H_7 } Y=S, Z=NO_2
3g, R=CH_3, **h**, R=C_2H_5, **i**, R=i-C_3H_7 } Y=O, Z=CH_3
j, R=CH_3, **k**, R=C_2H_5, **l**, R=i-C_3H_7 } Y=S, Z=CH_3

The structure of the 2-nitro-derivatives (**3a**—**f**) was confirmed by analytical and spectral data, and *via* treatment with methanolic potassium hydroxide to give the corresponding allenes namely, 1,1-bis-(*p*-alkoxyphenyl)-2-[xanthen(or thioxanthen)-9-ylidene]ethylenes (**4**) which were identical with the allenes previously obtained[1] by dehydrohalogenation of compounds **3** (Z=Br or Cl).

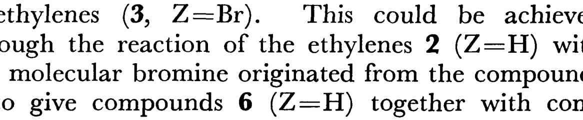


3a—**f**

methanolic KOH

4

It has been shown[1] that xanthenyl(or thioxanthenyl)-ethylenes (**3**, Z=H or Br), in the presence of hydrogen bromide, cleaved with bromine to give mainly xanthylium or thioxanthylium tribromide (**5**) and 2-bromoethylenes **6** (Z=H or Br). The 2-methyl, and 2-chloro-xanthenyl(or thioxanthenyl)-derivatives (**3**, Z=CH_3 or Cl) cleaved similarly to give compounds **5** and **6**.



5: Y=O, S

6: Z=CH_3, Cl

On the other hand, the tribromides (**5**) reacted with 1,1-bis-(*p*-alkoxyphenyl)ethylenes (**2**, Z=H) to afford mainly in each case the corresponding 1,1-bis-(*p*-alkoxyphenyl)-2-bromo-2-[xanthen(or thioxanthen)-9-yl]ethylenes (**3**, Z=Br). This could be achieved through the reaction of the ethylenes **2** (Z=H) with the molecular bromine originated from the compounds **5** to give compounds **6** (Z=H) together with compounds **7**. The latter reacted readily, *in situ*, to give, after spontaneous dehydrobromination of the inter-

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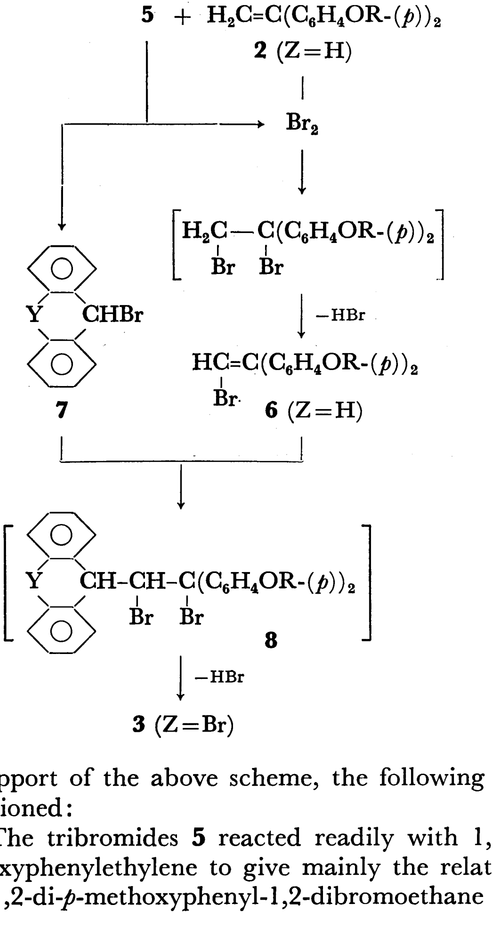
Table 1. 1,1-bis-(*p*-alkoxyphenyl)-2-nitro(and methyl)-2-[xanthen(and thioxanthen)-9-yl]ethylenes

Compd.	Mp (°C)	Mol formura	Microanalysis Found/Calcd			
			C	H	N	S
3a	152	$C_{29}H_{23}NO_5$	74.40 74.84	4.60 4.95	3.50 2.01	
b	147	$C_{31}H_{27}NO_5$			3.30 2.83	
c	164	$C_{33}H_{31}NO_5$			2.90 2.69	
d	148	$C_{29}H_{23}NO_4S$	72.70 72.35	5.10 4.78	3.20 2.91	6.70 6.65
e	150	$C_{31}H_{27}NO_4S$			2.90 2.75	6.40 6.29
f	180	$C_{33}H_{31}NO_4S$			2.80 2.60	6.30 5.69
g	104	$C_{30}H_{26}O_3$	82.40 88.95	5.80 5.99		
h	106	$C_{32}H_{30}O_3$	83.40 83.12	6.50 6.71		
i	147	$C_{34}H_{34}O_3$	83.50 83.27	6.80 6.94		
j	110	$C_{30}H_{26}O_2S$	79.70 80.00	5.50 5.78		7.20 7.11
k	120	$C_{32}H_{30}O_2S$	80.40 80.29	6.20 6.28		6.50 6.69
l	115	$C_{34}H_{34}O_2S$	80.50 80.63	6.90 6.72		6.30 6.32

mediate **8**, the 2-bromo-derivatives **3** (Z=Br).



In support of the above scheme, the following may be mentioned:

(i) The tribromides **5** reacted readily with 1,2-di-*p*-methoxyphenylethylene to give mainly the relatively stable 1,2-di-*p*-methoxyphenyl-1,2-dibromoethane and the corresponding xanthenyl (or thioxanthenyl) bromide (**7**).

(ii) When treated with excess dimethylaniline, for one minute, the tribromides **5** afforded *p*-bromodimethylaniline together with 9-*p*-dimethylaminophenylxanthene(or thioxanthene).

(iii) It has been reported that compounds **5**[2,3] lost their halogen when treated with alkali or hydroxylic solvents, to give xanthene(or thioxanthene) and xanthone(or thioxanthone).

(iv) Xanthenyl(or thioxanthenyl) bromide (**7**) was added readily to 1,1-bis-(*p*-methoxyphenyl)-2-bromoethylene (**6**, Z=H) at room temperature or at −5 °C to give compound **3** (Z=Br).

Experimental

All melting points are uncorrected. The infrared spectra were recorded with a Pye-Unicam SP 1000 spectrophotometer.

*1,1-Bis-(*p*-alkoxyphenyl)-2-nitroethylenes (2a—c).* A mixture of each of 1,1-bis-(*p*-alkoxyphenyl)-2-bromoethylene (0.01 mol), silver nitrite (0.03 ml) and acetone (50%, 100 ml) was heated to boiling for 10 hr and then filtered while hot. The filtrate was cooled and the product was collected and purified by crystallization from 80% ethanol. Yields: 80, 75 and 60% respectively. **2a** Mp and mixed mp[4] 112 °C. Found: C, 67.12; H, 5.42; N, 4.72%. Calcd for $C_{16}H_{15}NO_4$: C, 67.36; H, 5.26; N, 4.91%. **2b** Mp 65 °C. Found: C, 69.35; H, 5.82; N, 4.87%. Calcd for $C_{18}H_{19}NO_4$: C, 69.00; H, 6.07; N, 4.50%. **2c** Mp 102 °C. Found: C, 69.95; H, 6.62; N, 3.91%. Calcd for $C_{20}H_{23}NO_4$: C, 70.38; H, 6.74; N, 4.10%.

*1,1-Bis-(*p*-isopropoxyphenyl)-2-methylethylene (2f).* 0.1 mol of *p,p'*-di-isopropoxybenzophenone was added to a solution of methylmagnesium iodide (0.2 mol) in dry ether (100 ml) and the mixture was left overnight. The reaction mixture was decomposed with a cold solution of ammonium chloride. The ethereal layer was separated, washed with water, dried (Na_2SO_4) and filtered. The solvent was recovered and the oily product was distilled *in vacuo* to give **2f**, Bp 120 °C /20 Torr. Found: C, 80.48; H, 8.12%. Calcd for $C_{21}H_{26}O_2$: C, 80.13; H, 8.39%.

*1,1-Bis-(*p*-alkoxyphenyl)-2-nitro(or methyl)-2-[xanthen(or thioxanthen)-9-yl]ethylenes (3a—l).* Ten mmol of each of compounds **2a**—**f** was added to a solution of ten mmol of each of xanthenyl and thioxanthenyl chlorides (**1a**, **b**) in ether (100 ml) (prepared by passing hydrogen chloride through a cold ethereal solution of 9-xanthenol[5] or 9-thioxanthenol[6] till saturation). The mixture was left overnight. Ether was distilled off and the product was crystallized from ethanol to give the corresponding derivatives **3a**—**l** (Table 1).

Yields: 50—60%. IR for each of compounds **3a**—**f**: 2990 (CH), 1525 and 1360—1290 (NO_2) cm^{-1}.

*1,1-Bis-(*p*-alkoxyphenyl)-2-[xanthen(or thioxanthen)-9-ylidene]-ethylene (4).* A solution of each of the 2-nitro-derivatives **3a**—**f** (1 g) in methanolic potassium hydroxide (2 g in 100 ml) was heated to boiling (water-bath) for 5 hr, cooled, diluted with water and extracted with ether. The solvent was washed with water, dried (Na_2SO_4) and recovered. The residue was crystallized from ethanol–ether to give almost colorless crystals identified (mp and mixed mp[1]) as compounds **4a**—**f**. Yield 90%.

Reactions of Bromine with Compounds 3. *(a) With 1,1-Bis-(*p*-alkoxyphenyl)-2-methyl-2-[xanthen(or thioxanthen)-9-yl]ethylenes (3g—l)*: (i) Bromine (1.6 g, 0.01 mol) in chloroform (5 ml) was added to a solution of compound **3** g (2.17 g, 0.005 mol) in the same solvent (20 ml) which was previously saturated with hydrogen bromide. Instantaneous deep orange precipitate of xanthylium tribromide (2.1 g), mp and mixed mp²⁾ 164 °C, was formed. The filtrate was evaporated *in vacuo* and the residue was crystallized from ethanol to give colorless crystals (1.5 g) identified (mp and mixed mp⁷⁾) as 1,1-bis-(*p*-methoxyphenyl)-2-bromo-2-methylethylene.

(ii) The repetition of (i) using compound **3h** (2.25 g, 0.005 mol) gave thioxanthylium tribromide (2.2 g) as scarlet-red precipitate, mp and mixed mp³⁾ 185 °C, and 1,1-bis-(*p*-methoxyphenyl)-2-bromo-2-methylethylene (1.5 g).

(iii) The same reaction above using **3j** or **k** (0.005 mol) gave xanthylium tribromide (2.1 g) or thioxanthylium tribromide (2.2 g) together with, in each case, 1,1-bis-(*p*-ethoxyphenyl)-2-bromo-2-methylethylene (1.7 g), mp 71 °C. Found: C, 63.50; H, 5.46; Br, 22.20%. Calcd for $C_{19}H_{21}BrO_2$: C, 63.16; H, 5.81; Br, 22.16%.

*(b) With 1,1-Bis-(*p*-alkoxyphenyl)-2-chloro-2-[xanthen(or thioxanthen)-9-yl]ethylenes (6, Z=CH₃ or Cl).* When the above experiments (a; i, ii, iii) were repeated using the corresponding *p*-methoxy (or ethoxy)-2-chloro-derivatives (0.005 mol), similar results were obtained. Thus in each case the corresponding xanthylium tribromide (2.1 g) or thioxanthylium tribromide (2.2 g) together with 1,1-bis-(*p*-methoxyphenyl)-2-bromo-2-chloroethylene (1.6 g), mp and mixed mp⁸⁾ 103 °C or 1,1-bis(*p*-ethoxyphenyl)-2-bromo-2-chloroethylene, mp and mixed mp⁸⁾ 115 °C, were isolated respectively.

(c) When the above experiments, (a) and (b), were carried out using equimolecular quantities of bromine (0.005 mol), the same products were obtained together with unchanged derivatives equal to half the quantities of the corresponding starting materials.

*Reaction of Xanthylium(or thioxanthylium)-tribromide (5) with 1,1-Bis-(*p*-alkoxyphenyl)ethylenes (2, Z=H).* Compound **6** (0.005 mol) was added to a solution of each of the ethylenes **2**, (Z=H) (0.005 mol) in chloroform (50 ml) and the whole mixture was heated to boiling (water-bath) for 3 hr. The solvent was recovered and the residue was crystallized from ethanol to give colorless crystals identified (mp and mixed mp⁹⁾) as 1,1-bis-(*p*-alkoxyphenyl)-2-bromo-2-[xanthen-9-yl]-ethylene (**3**, Z=Br) respectively. Yield 90%.

When the above experiments were repeated using compound **5** (Y=S) (0.005 mol), 1,1-bis-(*p*-alkoxyphenyl)-2-bromo-2-[thioxanthen-9-yl]ethylene with mp which showed no depression when mixed with authentic samples¹⁾ was obtained. Yield 85%.

*Reactions of 5 with 1,2-Di-(*p*-methoxyphenyl)ethylene.* (a) A mixture of compound **5** (Y=O) (2.1 g) (0.005 mol), 1,2-di-(*p*-methoxyphenyl)ethylene (1.2 g) and chloroform (50 ml) was heated to boiling for 1 hr. The solvent was concentrated, diluted with petrol (60—80 °C) and cooled to give 1,2-dibromo-1,2-di-(*p*-alkoxyphenyl)ethane (1.9 g), mp and mixed mp¹⁰⁾ 178 °C. The filtrate was concentrated till near dryness and the residue was crystallized from dry petrol (40—60 °C) to give xanthenyl bromide (**7**) (1 g), mp and mixed mp²⁾ 87 °C.

(b) Repetition of experiment (a) using compound **5** (Y=S) (2.18 g, 0.005 mol) gave the 1,2-dibromo-1,2-di-(*p*-methoxyphenyl)ethane (1.9 g) and thioxanthenyl bromide (1.1 g).

Reactions of 5 (Y=O, S) with Dimethylaniline. A mixture of compound **5** (Y=O or S) (1 g) and dimethylaniline (10 ml) was heated to boiling for 1 min, cooled, made alkaline with aqueous sodium hydroxide and then steam-distilled. In each case, dimethylaniline passed over followed by *p*-bromodimethylaniline (0.3 g), mp and mixed mp¹¹⁾ 55 °C. The non-steamable portion was cooled and filtered off. The product was crystallized from ethanol to give 9-*p*-dimethylaminophenylxanthene (0.6 g), mp and mixed mp¹²⁾ 157 °C, or 9-*p*-dimethylaminophenylthioxanthene (0.6 g), mp 175 °C. Found: N, 4.72; S, 9.94%. Calcd for $C_{21}H_{19}NS$: N, 4.41; S, 10.09%.

Addition of Xanthenyl Bromide (7) to Compound 6 (Z=H). Xanthenyl bromide (0.005 mol) in chloroform (20 ml) was added to a solution of compound **6** (Z=H, R=MeO) (0.005 mol) in chloroform (20 ml) cooled to −5 °C. The reaction mixture was kept at −5 °C for 1 hr and then chloroform was washed with cold sodium hydroxide solution (5%), water, dried, filtered and recovered. The residue was crystallised from ethanol to give colorless crystals identified (mp and mixed mp¹⁾) as 1,1-bis-(*p*-methoxyphenyl)-2-bromo-2-[xanthen-9-yl]ethylene. Yield 40%.

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