(*c*) *From 9-α-bromoethylacridine* (VIII). Warming VIII hydrobromide on the steam bath with excess piperidine and washing the reaction mixture yielded the insoluble XI, m.p. 134–135°.

(*d*) *From 9-β-chloroethylacridine.* Following the procedure used by Eisleb with IX, we obtained pale yellow crystals of XI from acetone, m.p. 133°.

(*e*) *From 9-β-bromoethylacridine* (IX). Eisleb's procedure was repeated. The resultant XI melted at 135–136°.

By repeated crystallization, all of these XI specimens can be brought to melting point 135–137° and upon admixture with material from (*a*) no melting point depression is observed. With picric acid we obtained a material which sintered at 180° and melted at 218–220°. Monti reported the dipicrate to melt at 138–140°.

Acknowledgment. Microanalyses were performed by Betty Mount and Charles Kinser.

BETHESDA 14, MD.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, FACULTY OF SCIENCE, UNIVERSITY OF CAIRO]

Thermochromism of Dixanthylenes. Reactions with Substituted Xanthones. III[1a]

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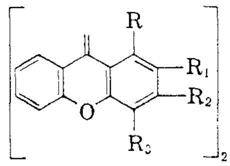
Substitution in dixanthylene (Ie) in position 1 and 1′, which hinders the planarity of the whole molecule, is detrimental to the development of thermochromic properties (Table 1). Fission of the central ethylene linkage in dixanthylenes is brought about by the action of thionyl chloride followed by water to give the xanthone derivatives (Va–d) and by the action of sulfur at 270° to yield the corresponding xanthione derivatives (VI, Table III). The new xanthone derivative Vc, needed in this investigation has been synthesized. 1-Chloroxanthone (Va) condenses with aromatic thiols in the presence of potassium hydroxide to yield the corresponding arylmercapto derivatives (VIII, Table IV) which are oxidized readily to the corresponding sulfone derivatives (IX, Table IV). Photochemical dehydrogenation of 2-methylxanthene is effected by the action of Vb and/or Vg–h. 9-Phenyl-4-chloroxanthene (Xb) undergoes photochemical oxidation in sunlight in the presence of oxygen, yielding 4-chloro-9-phenylxanthyl peroxide (XIb). Reduction of substituted xanthones with lithium aluminum hydride and with metallic sodium and alcohol led to the formation of the reduction products, listed in Table V.

In continuation of the study of the constitutional changes in thermochromic substances,[1] we now have extended our previous investigations[1(a)] to show how substitution affects the thermochromic properties of dixanthylene (Ie) a strongly thermochromic substance. The crystals are colorless at liquid air temperature, turn blue-greenish on heating and the melt is deep blue-green. The results are shown in Table I. The substances were tested in boiling diphenyl ether or anisole solutions.

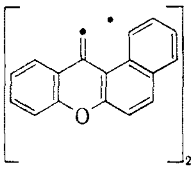
TABLE I

THERMOCHROMIC PROPERTIES

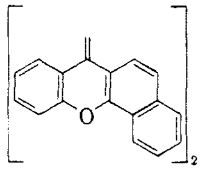
	R	R_1	R_2	R_3	
(a)	Cl	H	H	H	Very weakly thermochromic
(b)	CH_3	H	H	CH_3	Not thermochromic[1(a)]
(c)	CH_3	H	CH_3	H	Not thermochromic[1(a)]
(d)	Cl	H	H	CH_3	Not thermochromic[1(b)]
(e)	H	H	H	H	Strongly thermochromic[1(c)]
(f)	H	Br	H	H	Strongly thermochromic[1(a)]
(g)	H	Cl	H	H	Strongly thermochromic[1(b)]
(h)	H	CH_3	H	H	Strongly thermochromic
(i)	H	C_6H_5	H	H	Strongly thermochromic
(j)	H	H	H	Br	Strongly thermochromic[1(a)]
(k)	H	H	H	Cl	Strongly thermochromic[1(b)]
(l)	H	H	H	CH_3	Strongly thermochromic
(m)	H	CH_3	CH_3	H	Strongly thermochromic[1(a)]
(n)	H	CH_3	H	CH_3	Strongly thermochromic[1(a)]



I



(Weakly thermochromic)
II



(Strongly thermochromic)
III

DISCUSSION

Recently, Schönberg, Mustafa, and Asker[1(d)] advanced a hypothesis that "in overcrowded molecules in which planarity is hindered, the degree of non-planarity changes with temperature. This is associated with the change of color, one reason being that resonance is related to planarity." Dixanthylenes, *e.g.*, Ie, a thermochromic compound, lose this property upon substitution at position 1 and 1′ (*cf.* Table I). The loss of the thermochromic properties is due to a constitutional change in I, overcrowding of the molecule to such a degree that planarity is hindered even at high

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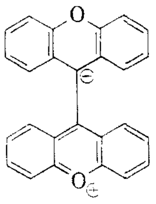
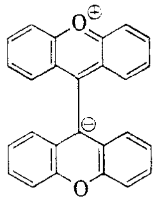
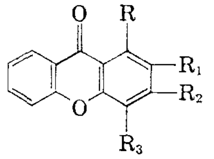
(1) (a) For part II *cf.* A. Mustafa, and M. E. D. Sobhy, *J. Am. Chem. Soc.*, **77**, 5124 (1955). (b) A. Schönberg, A. Mustafa, and M. E. D. Sobhy, *J. Am. Chem. Soc.*, **75**, 3377 (1953). (c) A. Schönberg and W. Asker, *J. Chem. Soc.*, 725 (1942). (d) A. Schönberg, A. Mustafa, and W. Asker, *J. Am. Chem. Soc.*, **76**, 4134 (1954).

temperatures.[2] In accordance with this conception is the lack of thermochromic properties of Ib–d and the weakly thermochromic properties of Ia and II since their molecules are much less overcrowded. From this, it has been concluded that the green forms of Ie and its analogs, "the colored molecules" have a greater degree of planarity; the experiments of thermochromic bianthrones have led Hirshberg, Loewenthal, Bergmann, and Pullman[3] to a similar conclusion.

Action of thionyl chloride on dixanthylenes. Dixanthylene shows remarkable behavior toward thionyl chloride, followed by the action of water.[1(c)] Fission of the central ethylene bond, which has single bond character (*cf.* IVa and IVb), occurs and xanthone is formed. We have now found that, analogously, the substituted xanthones (Va–d) are obtained by the action of thionyl chloride on the corresponding dixanthylenes followed by treatment with water.

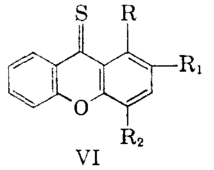

IVa


IVb



Va. $R = Cl; R_1 = R_2 = R_3 = H$
b. $R = H; R_1 = CH_3; R_2 = R_3 = H$
c. $R = H; R_1 = C_6H_5; R_2 = R_3 = H$
d. $R = R_1 = R_2 = H; R_3 = CH_3$
e. $R = R_3 = CH_3; R_1 = R_2 = H$
f. $R = R_2 = CH_3; R_1 = R_3 = H$
g. $R = R_2 = H; R_1 = R_3 = CH_3$
h. $R = R_3 = H; R_1 = R_2 = CH_3$

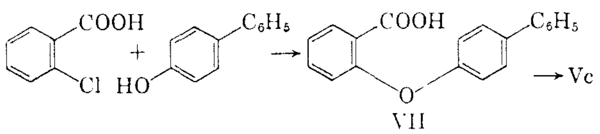
Action of sulfur on dixanthylenes. Treatment of the corresponding dixanthylenes with sulfur at 270° for a few minutes effects fission of the central ethylene bond[1(a)] with the formation of the substituted xanthiones (VI; *cf.* Table III).


VI

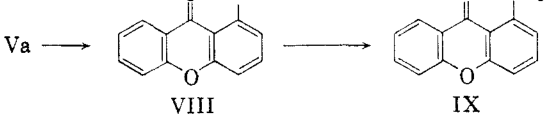
Methods of preparation. (a). *Dixanthylenes.* The dixanthylene derivatives listed in Table II were prepared by treating the corresponding xanthone derivatives with thionyl chloride, followed by the action of copper bronze,[1(a)] and by the action of copper bronze on the corresponding xanthiones.[1(a)] They also have been obtained by treating the corresponding xanthones with zinc dust and acetic acid in the presence of concentrated hydrochloric acid.[1(a)]

(b). *Xanthiones.* The xanthiones, listed in Table III, were prepared as mentioned above and by the action of phosphorus pentasulfide on the corresponding xanthones.[1(a)] They also have been obtained by the action of thiolacetic acid on the product obtained by the action of thionyl chloride on the corresponding xanthones.

(c). *Xanthones.* The new 2-phenylxanthone (Vc), needed in this work was prepared by the method of Dahr,[4] from *p*-hydroxydiphenyl and *o*-chlorobenzoic acid in the presence of sodium methoxide and copper powder, followed by ring closure of the intermediate phenoxybenzoic acid (VII) with sulfuric acid.



Reactions of 1-chloroxanthone (Va) with aromatic thiols. In conjunction with a study of pharmacological action of sulfur-containing compounds against *Bilharziasis*,[5] the action of thiolate anion on Va now has been investigated. The lability of the halogen in halogenated xanthones was previously demonstrated.[6] When a solution of Va in amyl alcohol is heated with the appropriate thiol in the presence of solid potassium hydroxide, the corresponding arylmercapto derivatives (VIII; Table IV) are obtained which are readily oxidized to the corresponding sulfone derivatives (IX; Table IV).


VIII IX

Photochemical reactions. In continuation of some recent work,[7] we now have found that Vb effects a

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[2] A. Schönberg and M. M. Sidky, *J. Am. Chem. Soc.*, **81**, 2259 (1959).

[3] Y. Hirshberg, E. Loewenthal, E. D. Bergmann, and B. Pullman, *Bull. soc. chim.*, (5) **18**, 88 (1951).

[4] S. N. Dahr, *J. Chem. Soc.*, **117**, 1053 (1920).

[5] (a) A. Mustafa, A. H. E. Harhash, and M. Kamel, *J. Am. Chem. Soc.*, **77**, 3860 (1955). (b) A. Mustafa, W. Asker, and M. E. D. Sobhy, *J. Am. Chem. Soc.*, 5121 **77**, (1955).

[6] *Cf.* the replacement reaction with thiolate anion (ref. 5(b)), with phenols [A. M. V. Dem Knesebeck and F. Ullmann, *Ber.*, **55**, 306 (1922)], anilines [H. Mauss, *Chem. Ber.*, **81**, 19 (1948)], aliphatic amines [S. Archer, L. B. Rochester, and M. Jackman, *J. Am. Chem. Soc.*, **76**, 588 (1954)], and alkylenediamines [S. Archer and C. M. Suter, *J. Am. Chem. Soc.*, **74**, 4206 (1952)].

[7] A. Mustafa, A. H. E. Harhash, A. K. E. Mansour, and S. M. A. R. Omran, *J. Am. Chem. Soc.*, **78**, 306 (1956).

TABLE II

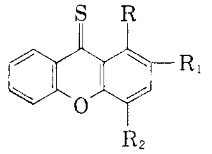
SUBSTITUTED DIXANTHYLENES

Dixanthylene[b,c]	M.P.[d]	Method of Preparation	Yield, %	Formula	Analyses Carbon, % Calcd.	Analyses Carbon, % Found	Analyses Hydrogen, % Calcd.	Analyses Hydrogen, % Found
Ia	277	(B)	27	$C_{28}H_{14}O_2Cl_2$[e]	72.73	72.78	3.26	3.22
Ih	262[a]	(A)	73	$C_{28}H_{20}O_2$	86.60	86.61	5.15	5.13
		(B)	34					
		(C)	59					
Ii	Above 300	(A)	71	$C_{38}H_{24}O_2$	89.06	89.04	4.69	4.65
		(B)	32					
		(C)	55					
Il	246[a]	(A)	69	$C_{28}H_{20}O_2$	86.60	86.58	5.15	5.10
		(B)	29					
		(C)	57					

[a] Deep bluish green melt. [b] An orange-red color is developed when treated with sulfuric acid at 100°. [c] Xylene was used as a solvent for crystallization. The dixanthylenes are easily soluble in hot anisole, but difficultly soluble in alcohol. [d] Melting points are uncorrected. [e] *Anal.* Calcd.: Cl, 16.55. Found: Cl, 16.58.

TABLE III

SUBSTITUTED XANTHIONES OBTAINED USING METHOD (a)

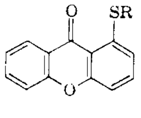
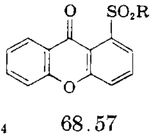


Xanthione Derivatives R	R₁	R₂	M.P.[a]	Temp. of Reaction	Yield, %	Formula	Analyses Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Sulfur, % Calcd.	Sulfur, % Found
Cl	H	H	142	90	82	$C_{13}H_7OSCl$[b]	63.29	63.27	2.84	2.81	12.98	12.70
H	CH_3	H	129	115	76	$C_{14}H_{10}OS$	74.34	74.30	4.42	4.41	14.16	14.13
H	C_6H_5	H	152	140	73	$C_{19}H_{12}OS$	79.17	79.14	4.17	4.13	11.11	11.08
H	H	CH_3	124	110	80	$C_{14}H_{10}OS$	74.34	74.31	4.42	4.46	14.16	14.12

[a] Melting points are uncorrected. The melt is green. [b] *Anal.* Calcd.: Cl, 14.40. Found: 14.29.

TABLE IV

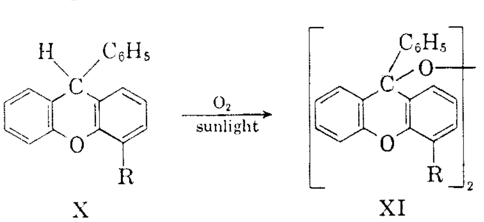
ARYLMERCAPTO DERIVATIVES

R	M.P.[a]	Yield, %	Formula	Analyses Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Sulfur, % Calcd.	Sulfur, % Found
									
C_6H_5	113	73	$C_{19}H_{12}SO_2$	75.00	75.02	3.95	3.92	10.53	10.50
o-$CH_3C_6H_4$	170	69	$C_{20}H_{14}SO_2$	75.47	75.43	4.40	4.38	10.06	10.02
p-$CH_3C_6H_4$	129	77	$C_{20}H_{14}SO_2$	75.47	75.49	4.40	4.37	10.06	10.09
m-$CH_3C_6H_4$	164	62	$C_{20}H_{14}SO_2$	75.47	75.46	4.40	4.41	10.06	10.03
									
o-$CH_3C_6H_4$	202	71	$C_{20}H_{14}SO_4$	68.57	68.53	4.00	4.03	9.14	9.11
p-$CH_3C_6H_4$	207	73	$C_{20}H_{14}SO_4$	68.57	68.57	4.00	4.38	9.14	9.10
m-$CH_3C_6H_4$	196	66	$C_{20}H_{14}SO_4$	68.57	68.56	4.00	4.01	9.14	9.13

[a] Melting points are uncorrected.

photochemical dehydrogenation reaction,[8] yielding 2,2′-dimethyl-9,9′-bixanthene when its benzene solution is allowed to react with 2-methyl xanthene in sunlight and in the absence of oxygen. A similar photochemical dehydrogenation reaction has also been observed, yielding 2,2′-dimethyl-9,9′-bixanthene, when Vd, Vg, and/or Vh was used instead of Vb in the above reaction. The fate of the ketone has not yet been established.

9-Arylxanthenes, *e.g.*, 9-phenylxanthene (Xa), when their benzene solutions are exposed to sunlight in presence of air, form 9-arylxanthyl peroxides, *e.g.*, 9-phenylxanthyl peroxide (XIa).[5(b)] We now have found that Xb behaves, similarly, under the action of sunlight in the presence of oxygen, yielding 4-chloro-9-phenylxanthyl peroxide (XIb). Xb now has been obtained by the reduction of 4-chloro-9-phenylxanthhydrol with zinc and glacial acetic acid. The photoperoxide formation of XI under the influence of sunlight possibly may be attributed to a direct attack by oxygen on an excited form of X. That XIb is a peroxide is established by the fact that it liberates iodine from potassium iodide solution in acetic acid; XIb gives 4-chloroxanthone on pyrolysis.



X XI

a. R = H; b. R = Cl

Reactions with lithium aluminum hydride. It been found that when certain aromatic ketones containing amino or methoxyl groups *ortho* or *para* to the carbonyl group are reduced under forcing conditions with excess lithium aluminum hydride at elevated temperature for long periods, reduction and hydrogenolysis occur to a methyl or methylene group.[9] Recently, similar behavior has been reported in the xanthone series. Thus, reduction of xanthone, 1,2-benzo-, and 3,4-benzoxanthones[10] and 10-thioxanthone with lithium aluminum hydride proceeds one step further to give the corresponding xanthenes.[11] Halogen substituted xanthones, *e.g.*, 2-chloro- and 4-chloroxanthones undergo reduction with the same reagent leading to the formation of xanthene in every case with the loss of halogen.[5(b)] The reduction of hydroxyxanthones, *e.g.*, 1-hydroxy- and 1-hydroxy-3-methylxanthone with the same reagent gives the corresponding xanthene derivatives, namely, 1-hydroxy- and 1-hydroxy-3-methylxanthene.[9] In none of the examples cited does fractional crystallization of the reaction products reveal the presence of the corresponding hydrols.[12] The reaction was carried out in all cases in boiling ether-benzene solution.

We now have investigated the reduction of a number of mono- and disubstituted xanthones with lithium aluminum hydride. Thus, when Vd–g are allowed to react with the same reagent in boiling ether-benzene solution for three hours and kept at room temperature overnight, followed by hydrolysis, the corresponding xanthhydrol derivatives, namely, 4-methyl-, 1,4-dimethyl-, 1,3-dimethyl- and 2,4-dimethylxanthhydrols (*cf.* Table V), are obtained, respectively, in an almost quantitative yield. Fractional crystallization of the reaction products does not reveal the presence of the corresponding xanthones. On the other hand, when Vb–c are treated with the same reagent under the same conditions, the corresponding xanthene derivatives, namely, 2-methyl- and 2-phenylxanthenes (*cf.* Table V) are obtained, respectively, in an almost quantitative yield.

The reduction of Vh with lithium aluminum hydride under the same conditions, led to the formation of a colorless product which upon fractional crystallization gave 2,3-dimethylxanthhydrol and 2,3-dimethylxanthene. We would like to report that, whereas, the 1- or 4-monosubstituted or the 1,4-disubstituted xanthones give the corresponding xanthhydrol derivatives on reduction with lithium aluminum hydride, the 2-substituted xanthones give the corresponding xanthene derivatives with the same reagent. Vh, on reduction with lithium aluminum hydride, gives a mixture of the corresponding xanthhydrol and xanthene derivatives. The study of the effet of substituent group[13] on the reduction of the xanthone derivatives with lithium aluminum hydride, under different experimental conditions, is under further investigation.

Treatment of Vc with metallic sodium and alcohol[14] gives the same reduction product, obtained by

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[8] *Cf.* the photochemical dehydrogenation of diphenylmethane and anthrone by xanthone to give tetraphenylethane and 10,10′-bianthrone respectively (A. Schonberg and A. Mustafa, *J. Chem. Soc.*, **67** (1944); *Chem. Revs.*, **40**, 181 (1947)) and the photochemical dehydrogenation of xanthene by 4-chloroxanthone yielding 9,9′-bixanthene (ref. 5b).

[9] For references, *cf.* A. Mustafa and O. H. Hishmat, *J. Org. Chem.*, **22**, 1644 (1957).

[10] A. Mustafa and M. K. Hilmy, *J. Chem. Soc.*, 1343 (1952).

[11] *Cf.* the reduction of decussatin methyl ether (1,2,5,6-tetramethoxyxanthone) to the xanthene derivative when boiled with excess lithium aluminum hydride in ether for twelve hours (R. C. Shah, A. B. Kulkarni, and C. G. Joshi, *J. Sci. Ind. Research (India)*, **13B**, 186 (1954).

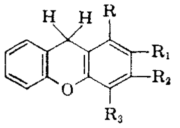
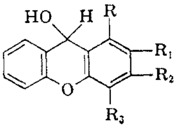
[12] *Cf.* the reduction of xanthone to xanthhydrol with the same reagent (P. Mirza and R. Robinson, *Nature*, **166**, 997 (1950) and the reduction of 1-chloro-4-methylxanthone to 1-chloro-4-methylxanthhydrol [ref. 6(b)].

[13] *Cf.* the effect of substituent in the 6-position on the ready reduction of 6-hydroxylbenzanthrone with lithium aluminum hydride, in contrast to the stability of the unsubstituted benzanthrone toward the same reagent [H. E. Zeiger and J. A. Dixon, Division of Organic Chemistry of the American Chemical Society, Abstracts of papers presented at Atlantic City, N. J., Sept. 13 to 18, 1959, (p. 19P).]

[14] J. Heller and St. Kostanecki, *Ber.*, **41**, 1325 (1908).

TABLE V

THE REDUCTION PRODUCTS OF SUBSTITUTED XANTHONES (Va–h)

Xanthone Derivative	Reduction Product				Method of Reduction	Yield, %	M.P.[c]	Solvent for Cryst.[f]	Formula	Analyses			
										Carbon, %		Hydrogen, %	
	R	R₁	R₂	R₃						Calcd.	Found	Calcd.	Found
													
Va	H	H	H	H	(b)	71	101	A	$C_{13}H_{10}O$	85.73	85.71	5.49	5.51
Vb	H	CH_3	H	H	(a)	62	98	A	$C_{14}H_{12}O$	85.71	85.63	6.12	6.10
Vc	H	C_6H_5	H	H	(a) and (b)	71, 79	130	A	$C_{19}H_{14}O$	88.37	88.33	5.43	5.37
Vh	H	CH_3	CH_3	H	(a) and (b)[3]	22, 78	124	A	$C_{15}H_{14}O$	85.71	85.73	6.67	6.62
													
Vd	H	H	H	CH_3	(a)	61	142	C	$C_{14}H_{12}O_2$[d]	79.25	79.17	5.66	5.69
Ve	CH_3	H	H	CH_3	(a) and (b)	73, 64	204	B	$C_{15}H_{14}O_2$	79.65	79.60	6.19	6.23
Vf	CH_3	H	CH_3	H	(a)	67	201	B	$C_{15}H_{14}O_2$	79.65	79.59	6.19	6.22
Vg	H	CH_3	H	CH_3	(a)	58	152	C	$C_{15}H_{14}O_2$	79.65	79.61	6.19	6.20
Vh	H	CH_3	CH_3	H	(a)[e]	42	208	B	$C_{15}H_{14}O_2$	79.65	79.61	6.19	6.24

[a] Reduction with lithium aluminum hydride. [b] Reduction with sodium and alcohol. [c] Melting points are uncorrected. [d] Mol. wt., calcd.: 212. Found: 220. [e] For the separation of 2,3-dimethylxanthene and 2,3-dimethylxanthhydrol, the reaction product was triturated with boiling alcohol, in which the xanthene derivative is soluble. [f] A is ethyl alcohol, B is benzene, and C is benzene-petroleum ether.

the action of lithium aluminum hydride on Vc. On the other hand, the reduction of Vh with metallic sodium and alcohol yields only 2,3-dimethylxanthene. Treatment of Va with metallic sodium and alcohol effects the formation of xanthene with the loss of halogen.[5(b)]

EXPERIMENTAL

Dixanthylene derivatives (I). *Method* (a). Two g. of the xanthone were refluxed (using a calcium chloride tube) with 15 ml. of thionyl chloride (or with 10 g. of oxalyl chloride) for 10 hr.; the excess thionyl chloride (or oxalyl chloride) was distilled, and the residual oil dissolved in 30 ml. of dry xylene and refluxed with 4 g. of copper bronze for 6 hr., with occasional shaking. The xylene solution was filtered while hot and concentrated; on cooling the dixanthylene derivative crystallized. (*cf.* Table II).

(b). One g. of the xanthone after 30 min. boiling with 0.5 g. of zinc dust and 15 ml. of glacial acetic acid in the presence of 2–3 drops of concd. hydrochloric acid gave the dixanthylene derivative.

(c). A solution of 1 g. of xanthione in 20 ml. of dry xylene was refluxed with 0.5 g. of copper bronze for 6 hr. The filtered xylene solution, on concentration, gave the dixanthylene derivative.

Dilute solutions of the dixanthylenes Ig,h,k in diphenyl ether or anisole are almost colorless at room temperature; the boiling solutions are bluish green; the color phenomenon is reversible.

Action of thionyl chloride. General procedure. A solution of 1 g. of the appropriate dixanthylene derivative in 30 ml. of thionyl chloride was refluxed for 6 hr.; the excess solvent was distilled completely (pump), and the residual oil was then dissolved in benzene and shaken with water at 30° for 30 min. The benzene layer was evaporated and the residual was crystallized from benzene-petroleum ether (b.p. 40–60°).

2-Chloroxanthone (Va) (melting point and mixed melting point and color reaction with sulfuric acid) was obtained in 73% yield.

Similar treatment of Ih with thionyl chloride gave 68% yield of 2-methylxanthone (Vb). 2-Phenylxanthone (Vc) was obtained in 66% yield from the corresponding dixanthylene derivative (Ii).

4-Methylxanthone (Vd) in 63% yield was, similarly, produced upon treatment of Il with thionyl chloride.

Action of sulfur. General procedure. One g. of the appropriate dixanthylene derivative was ground with 0.5 g. of sulfur and the mixture was heated at 270° (bath temperature) for 10 min., allowed to cool, powdered, and extracted repeatedly with hot petroleum ether (b.p. 60–80°). The extract was concentrated, cooled, filtered from precipitated sulfur, and the bluish green solution was further concentrated and cooled.

The xanthiones (VI, listed in Table III) were identified by melting point and mixed melting point determination with an authentic sample (see below) and by the formation of a reddish brown colored surface on the crystals of mercuric chloride added to their benzene solutions.[15]

Xanthiones. General procedure. (a). One g. of the xanthone was mixed thoroughly with 1.2 g. of phosphorus pentasulfide. The mixture was heated for 1 hr. and the solid mass, obtained on cooling, was powdered and extracted several times with hot benzene (*ca.* 50 ml.). The benzene solution was evaporated and the solid residue was dissolved in hot petroleum ether (b.p. 60–80°) and concentrated; on cooling, the xanthione derivative crystallized.

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(15) For the formation of molecular compounds between xanthione and mercuric chloride, *cf.* A. Schonberg, *Ber.*, **58**, 1793 (1925).

(b). The orange oil, obtained by the action of 15 ml. of thionyl chloride on 1 g. of the xanthone, as described above, was dissolved in 40 ml. of dry benzene and refluxed for 6 hr. with 2 ml. of thiolacetic acid during which time a deep bluish green color developed. The excess benzene and acid were removed by distillation and on addition of light petroleum (b.p. 40–60°) to the residue, the xanthione derivative was deposited; it was recrystallized from petroleum ether (b.p. 60–80°).

The xanthiones (listed in Table III) were easily soluble in benzene, giving a bluish green solution, but sparingly soluble in petroleum ether and gave an orange-red color with sulfuric acid.

Method (b) was applied in the case of 4-methyl-, 2-methyl-,[16] and 2-phenylxanthiones; the yields were 73, 66, and 63% respectively.

Action of aromatic thiols. General procedure. A solution of 2 g. of Va and 1.5 g. of the thiol in 25 ml. of amyl alcohol was treated with 0.1 g. of solid potassium hydroxide. The reaction mixture was refluxed for 3 hr. and kept overnight at room temperature. The yellow solid that separated was filtered, washed with cold ethyl alcohol, then with water and finally with cold acetone. It was extracted with hot petroleum ether (b.p. 60–80°, *ca.* 60 ml.) and the insoluble part was crystallized from glacial acetic acid.

The amylmercapto derivatives VIII (*cf.* Table IV) were oxidized to the corresponding sulfones (IX) as follows: A solution of 1 g. of the appropriate arylmercapto derivative in 25 ml. of glacial acetic acid was treated with 5 ml. of hydrogen peroxide (30%). The reaction mixture was heated (steam bath) for 1 hr. and kept overnight at room temperature. The resulting solid was crystallized from glacial acetic acid.

The sulfones IX (Table IV) are colorless, and easily soluble in hot xylene, but are sparingly soluble in cold ethyl alcohol and acetic acid. They give a pale yellow color with sulfuric acid.

Photochemical experiments. General remarks. The benzene was thiophene-free and dried over sodium. The reaction mixture was placed in a Schlenk tube[17] of pyrex glass, and the air then was displaced by dry carbon dioxide and the tube sealed by fusion.

The photoformation of peroxide was carried out as above, but in the presence of dry air. Control experiments in the dark, but otherwise under identical conditions, showed no reaction.

(a). *2-Methylxanthene*[18] *and* Vb. A solution of 1 g. of 2-methylxanthene and 1.3 g. of Vb in 30 ml. of benzene, after being exposed to sunlight for 10 days (July), acquired a green fluorescence, and the photoproduct separated during exposure as colorless crystals. These were collected, washed with cold benzene (*ca.* 10 ml.) and recrystallized from hot xylene. The yield of 2,2′-dimethyl-9,9′-bixanthene is 0.41 g. and melts at 250°.

Anal. Calcd. for $C_{28}H_{22}O_2$: C, 86.15; H, 5.64. Found: C, 86.21; H, 5.66.

It is almost insoluble in cold concd. sulfuric acid, but dissolves with difficulty at 100° giving an orange solution.

The above experiment was repeated using Vd, Vg, and/or Vh instead of Vb, and the above-mentioned compound was obtained in each case (*ca.* 4.0, 3.7, and 3.1 g., respectively) (identified by melting point and mixed melting point as 2,2′-dimethyl-9,9′-bixanthene).

(b). *9-Phenyl-4-chloroxanthene* (Xb) *and oxygen.* Xb was obtained in 65% yield upon reduction of 9-phenyl-4-chloroxanthhydrol[19] after the method of Ullmann and Engi.[20] It forms colorless crystals from petroleum ether (b.p. 40–60°), m.p. 114°. It is easily soluble in benzene and gives no color with sulfuric acid.

Anal. Calcd. for $C_{19}H_{13}ClO$: C, 77.98; H, 4.44; Cl, 12.13. Found: C, 77.80; H, 4.51; Cl, 12.10.

A solution of 1 g. of Xb in 30 ml. of benzene was exposed to sunlight for 15 days (May). The colorless crystals that separated during exposure were recrystallized from benzene (*ca.* 0.66 g.), m.p. 214° dec. (brown red melt).

Anal. Calcd. for $C_{38}H_{24}Cl_2O_4$: C, 74.15; H, 3.90; Cl, 11.54. Found: C, 74.31; H, 3.70; Cl, 11.35.

XIb is soluble in hot benzene and xylene, but difficultly soluble in ethyl alcohol and gives a yellowish green fluorescence with sulfuric acid.

Thermal decomposition of 0.5 g. of XIb for half an hour at 270° (bath-temp.) afforded 4-chloroxanthone (*ca.* 0.16 g.) (melting point and mixed melting point and color reaction with sulfuric acid) as a colorless sublimate.

Reduction of substituted xanthones: (a). *Lithium aluminum hydride. General procedure.* Solvents dried over sodium were used. To 0.7 g. of lithium aluminum hydride (New Metals and Chemicals, Ltd., London) was added 50 ml. of ether. After 15 min., a benzene solution (30 ml.) containing 1 g. of each of the appropriate xanthone (*cf.* Table V) was added in portions. The reaction mixture was refluxed for 3 hr. and then kept overnight at room temperature. After treatment with dilute hydrochloric acid the ethereal solutions were evaporated and the oily residues were solidified upon washing with light petroleum (b.p. below 40°) and crystallized from the proper solvent (*cf.* Table V).

(b). *Metallic sodium and alcohol.* A solution of 3 g. of each of the corresponding xanthone derivatives (*cf.* Table V) in 60 ml. of hot absolute ethyl alcohol was added dropwise to 7 g. of molten metallic sodium after the method described by Heller and Kostanecki.[14] The reaction mixture was steam distilled. The solid obtained from the distillate was crystallized from the appropriate solvent.

Xanthhydrol derivatives listed in Table V are sparingly soluble in petroleum ether (b.p. 50–70°) and difficultly soluble in ethyl alcohol. They give an orange-red color with sulfuric acid. The xanthene derivatives (*cf.* Table V) are easily soluble in benzene, sparingly soluble in cold ethyl alcohol, and give no color with sulfuric acid.

Preparation of 2-phenylxanthone (Vc). (a). A procedure similar to that described by Dahr[4] for the preparation of 2-chloroxanthone was used.

A mixture of 4.1 g. of *p*-hydroxydiphenyl, 3.2 g. of *o*-chlorobenzoic acid, 0.8 g. of metallic sodium, 20 ml. of methyl alcohol, and a trace of copper powder was heated gradually (oil bath) until all the alcohol evaporated. The reaction mixture was kept at 150° for half an hour and the temperature then was raised to 220°. It was cooled, powdered, and the solid was digested with dilute aqueous sodium hydroxide solution (8%, *ca.* 60 ml.). The filtered alkaline extract was acidified with cold dilute hydrochloric acid and the solid obtained was washed thoroughly with cold water, crystallized from ethyl alcohol, and finally from benzene. 2-(4-Phenylphenoxy)benzoic acid (VII), m.p. 147°, was obtained in 77% yield. It is easily soluble in hot benzene and alcohol and gives a yellow color with sulfuric acid.

Anal. Calcd. for $C_{19}H_{14}O_3$: C, 78.62; H, 4.83. Found: C, 78.60; H, 4.85.

VII (3 g.) was heated with 30 ml. of sulfuric acid (70%, stream bath) for 15 min. The cold reaction mixture was poured onto water and the solid substance that separated, was filtered, washed thoroughly with water, and crystallized from ethyl alcohol as colorless crystals (*ca.* 1.6 g.), m.p. 154°.

Anal. Calcd. for $C_{19}H_{12}O_2$: C, 83.82; H, 4.41. Found: C, 83.84; H, 4.40.

Vc is difficultly soluble in benzene and petroleum ether,

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(16) While this paper was in progress A. Schönberg and M. M. Sidky (ref. 2) described the preparation of 2-methyl- and 4-methylxanthiones by a similar procedure; the results are concordant.

(17) W. Schlenk and A. Thal, *Ber.*, **46**, 2655 (1913).

(18) R. G. McConnel, V. Petrow, and B. Sturgeon, *J. Chem. Soc.*, 812 (1956).

(19) M. Gomberg and S. H. Cone, *Ann.*, **370**, 183 (1909).

(20) F. Ullmann and E. Engi, *Ber.*, **37**, 2341 (1904).

soluble in boiling ethyl alcohol, and gives a yellow color with a green fluorescence when treated with sulfuric acid.

(b). Vb and Vd were prepared from the condensation of *p*-cresol and *o*-cresol with *o*-chlorobenzoic acid, respectively, as described above without the isolation of the intermediate substituted phenoxy-*o*-benzoic acid, and proved to be identical with samples, prepared after Ullmann and Zlokasoff[21]; the yield was 69% and 73%, respectively.

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[21] F. Ullmann and M. Zlokasoff, *Ber.*, **38**, 2111 (1905).

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF MINNESOTA]

Mixed Indole Dimers, Trimers, and Their Acyl Derivatives[1]

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The synthesis of the first mixed indole and indole:pyrrole dimers is described. They are derived from an A component (an indole having an open 2-position) and a B component (an indole or pyrrole more nucleophilic than the A component). Included are the dimers from indole with 2-methylindole (Ib), 1,2-dimethylindole (Ic), 2-phenylindole (Id), or 2,5-dimethylpyrrole (XIIa), and the dimer from skatole with 2-methylindole (IIIa). Structures are assigned on the basis of spectral data and by analogy with the proven structure of diindole (Ia). The competitive dimerization reaction of indole and 1-methylindole permitted isolation, after acylation with maleic anhydride, of only maleyldiindole (XVa). The competitive reaction of indole and skatole proceeded in rather clean-cut stepwise fashion with formation first of diindole hydrochloride and then of diskatole hydrochloride. A new homodimer, 1,3-dimethylindole dimer (VIb), has been prepared. Evidence is presented concerning the structure of diskatole (VIa). As byproducts in the preparation of the mixed dimers, the first mixed trimers have been prepared. Included are diindole:2-methylindole trimer (IIc); diindole:1,2-dimethylindole trimer (IId); and indole:di-2,5-dimethylpyrrole trimer (XIII). Diindole: 1,2-dimethylindole trimer (IId) is different from the dimethyltriindole obtained by methylation of triindole (IIa). Evidence is presented that, contrary to a previous report, the latter dimethyltriindole is in reality an *N,N*-dimethylaniline derivative (IIb) resulting from dimethylation of the primary amino group of triindole. Acyl derivatives of the mixed dimers and trimers have been prepared from maleic, succinic, itaconic, and citraconic anhydrides. Whereas acylation of diindole, indole:2-phenylindole dimer, and indole:2,5-dimethylpyrrole dimer with maleic anhydride gave only the maleyl derivatives, the corresponding reactions with indole:2-methylindole dimer and indole:1,2-dimethylindole dimer gave not only the maleyl derivatives (XVb–c) but also lesser amounts of the fumaryl derivatives (XVI b–c). In the two cases where both maleyl and fumaryl derivatives were obtained, hydrogenation of these stereoisomers gave the succinyl derivatives (XVIIb–c), which were also prepared independently by acylation of the dimers with succinic anhydride. Skatole:2-methylindole dimer with maleic anhydride gave the maleyl derivative (IIIb), but in more polar solvents an isomer was obtained to which the spiro indolenine structure XXI is assigned.

Mixed indole dimers and trimers. Although homodimers of indole,[4–7] skatole,[8,9] 1-methylindole,[10] and 7-methylindole[10] are known, and 2-methylindole dimer has been prepared by a method other than dimerization,[11] there appear to be no published reports of the synthesis of mixed indole dimers or their derivatives.[12] The mechanism proposed[6] for the formation of diindole (Ia) offered hope for the synthesis of mixed indole dimers. Requirements for indole dimerization appear to include a protonated indole with an open 2-position (which we shall designate as the A component) and an indole with a nucleophilic position, usually an open 3-position (B component). Consequently, although its dimer has been prepared by another synthetic route,[11] 2-methylindole does not undergo

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[2] We are indebted to the Graduate School of the University of Minnesota for a 1957 Faculty Summer Research Appointment.

[3] From the Ph.D. thesis of Charles F. Hammer, May 1959. Research Corporation Research Assistant 1956–1959, Upjohn Company Summer Fellow 1958. We are indebted to the Research Corporation for a Frederick Gardner Cottrell Grant in support of this research, and to the Upjohn Company for a summer fellowship.

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[12] Dr. G. F. Smith of the University of Manchester, England, has kindly informed us in a private communication (Nov. 22, 1957) that he has prepared a mixed diindolyl (corresponding to indole:2-methylindole dimer), the formation of which almost certainly involves an unstable mixed indole dimer as an intermediate: