*Anal.* Calcd. for $C_{23}H_{24}N_2$: C, 84.10; H, 7.37. Found: C, 84.10; H, 7.10.

**N-(3-Methyl-6-methylaminobenzyl)-*p*-toluidine Dibenzenesulfonamide (IV).**—Acetone was added to the filtrates from two of the above syntheses (R = $C_6H_5$, $CH_3$) to precipitate excess 2,4-dinitrophenylhydrazine reagent. The filtrate was made strongly basic with sodium hydroxide (20%) and excess benzenesulfonyl chloride added. The precipitate which formed after several hours of shaking was collected and recrystallized from ethanol, m.p. 159–161°.

*Anal.* Calcd. for $C_{22}H_{28}N_2S_2O_4$: C, 64.59; H, 5.42. Found: C, 64.73; H, 5.32.

**Manganese Dioxide Oxidation of 6-Methyl-3-*p*-tolyl-1,2,3,4-tetrahydroquinazoline.**—The tetrahydroquinazoline was prepared according to Eisner and Wagner[9] from formaldehyde and N-(2-amino-5-methylbenzyl)-*p*-toluidine. The product even when pure exhibited a variable m.p. from 141–151° possibly due to polymorphism. After one recrystallization from ethanol, the tetrahydroquinazoline (0.700 g.) was stirred with specially prepared manganese dioxide (1.5 g.)[8] in benzene–ether (1:1, 20 ml.) for 4 hours. The solvents were removed from the product with a current of dry nitrogen and the product was recrystallized from ligroin, m.p. 158° (0.558 g., 81%) alone or when mixed with authentic II.

BETHESDA, MD.

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

# Reactions with Halogen Substituted Xanthones. II[1]

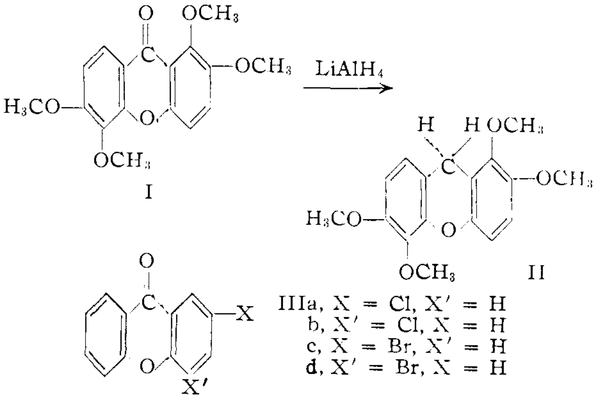
BY AHMED MUSTAFA, WAFIA ASKER AND MOHAMED EZZ EL-DIN SOBHY

RECEIVED APRIL 12, 1955

Reduction of halogen-substituted xanthones (IIIa-d) with lithium aluminum hydride and with metallic sodium and alcohol led to the formation of xanthene with loss of the halogen. The reduction of xanthone to xanthene with lithium aluminum hydride is discussed. Xanthones IVa-b and the thiaxanthone IVc with halogen in position 1 condense with aromatic thiols in the presence of potassium hydroxide, to yield the corresponding arylmercapto derivatives Va-c which are oxidized readily to the corresponding sulfone derivatives VIa-c. Whereas IIIa undergoes photochemical addition reaction with xanthene in sunlight to give the carbinol VIIb, IIIb effects the photochemical dehydrogenation of xanthene to 9,9′-bixanthene. 9-Phenyl-2-chloroxanthene (VIIIb) undergoes photochemical oxidation in sunlight in the presence of oxygen, yielding 9-phenyl-2-chloroxanthyl peroxide (IXb).

**(a) Reactions with Lithium Aluminum Hydride.**—Recently, Shah, Kulkarni and Joshi[2] have shown that when desussatin methyl ether (I), a naturally occurring xanthone, is boiled with excess of lithium aluminum hydride in ether for about 12 hours to give the xanthene derivative II, xanthone is reduced by this reagent to xanthydrol.[3] Mustafa and Hilmy[1] previously have reported that reduction of xanthones, *e.g.*, xanthone, 1,2-benzo- and 3,4-benzoxanthones, with the same reagent proceeds a step further to give the corresponding xanthenes[4] in an almost quantitative yield when the reaction was carried out in boiling ether–benzene solution.

We now have investigated the action of excess lithium aluminum hydride on halogen substituted xanthones, namely, 2-chloro- (IIIa), 4-chloro- (IIIb), 2-bromo- (IIIc) and 4-bromoxanthone (IIId) in boiling ether–benzene solution and have obtained xanthene in each case with the loss of halogen.[5] Similar results are obtained when IIIa-d are treated with metallic sodium and alcohol under the same experimental conditions by which xanthone is reduced to xanthene.[6,7]



I

II

IIIa, X = Cl, X′ = H
b, X′ = Cl, X = H
c, X = Br, X′ = H
d, X′ = Br, X = H

On the other hand, the reduction of 1-chloro-4-methylxanthone with lithium aluminum hydride under the same conditions, led, without loss of halogen, to the formation of a colorless product believed to be 1-chloro-4-methylxanthydrol. The formation of the hydrol and not the methylene derivative may be attributed to the precipitation phenomenon.[2,4]

**(b) Reactions with Aromatic Thiols.**—In conjunction with a study of pharmacological action of sulfur-containing compounds against bilharziasis,[8] the action of the thiolate anion on halogen substituted xanthones IVa-b and 1-chloro-4-methylthiaxanthone (IVc) now has been investigated. The lability of the halogen in halogenated xanthones was demonstrated by effecting a replacement reac-

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[1] For part I *cf.* A. Mustafa and Mustafa K. Hilmy, *J. Chem. Soc.*, 1343 (1952).

[2] R. C. Shah, A. B. Kulkarni and C. G. Joshi, *J. Sci. Ind. Res.*, **13B**, 186 (1954).

[3] *Cf.* R. Mirza and R. Robinson, *Nature*, **166**, 929, 997 (1950).

[4] Generally, carbonyl compounds are reduced to carbinols by lithium aluminum hydride. Scattered observations of further reduction of the carbinol to the methylene derivative have been reported. B. Witkop (THIS JOURNAL, **72**, 614 (1950)) observed hydrogenolysis of spiro-(cyclopentane-1,2′-dihydroindoxyl) to spiro-(cyclopentane-1,2′-dihydroindole). L. H. Conover and D. S. Tarbell (*ibid.*, **72**, 3586 (1950)) have shown that 4,4′-dimethoxybenzophenone and N,N-dialkyl-*p*-aminobenzophenone gave a considerable amount of 4,4′-dimethoxydiphenylmethane and of N,N-dialkyl-*p*-aminodiphenylmethane, respectively, on reduction with lithium aluminum hydride.

[5] *Cf.* the reduction of 2,7-dibromoxanthone (A. Lespagnol and B. Bertrand, *Bull. soc. chim.*, **10**, 50 (1943)) and of 2,7-diiodoxanthone (B. Bertrand and A. Lespagnol, *ibid.*, **15**, 428 (1948)) with aluminum isopropoxide to give the propyl ether of the xanthydrol derivative without the loss of halogen.

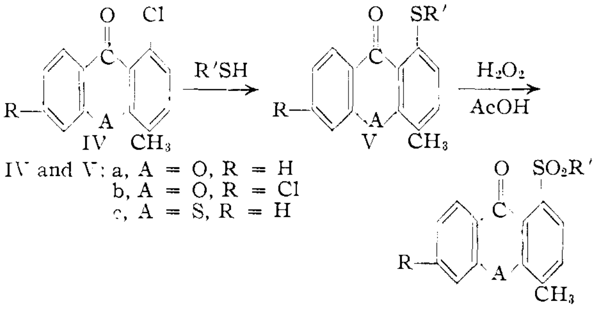
[6] J. Heller and St. v. Kostanecki, *Ber.*, **41**, 1325 (1908).

[7] This part was carried out with Mohamed Ezz El-Din Sobhy.

[8] A. Mustafa, A. H. E. Harhash and M. Kamel, THIS JOURNAL, **77**, 3860 (1955).

tion with phenols,[9] anilines,[10] aliphatic amines[11] and alkylenediamines.[12] IVc is sufficiently reactive to condense with an amine at elevated temperature.[11] When a solution of IVa, IVb and or IVc in amyl alcohol is heated with the appropriate thiol in the presence of solid potassium hydroxide, the corresponding arylmercapto derivatives (Va-c; *cf.* Table I) are obtained. Va-b are oxidized readily to the corresponding sulfone derivatives (VIa-b) (*cf.* Table I); oxidation of Vc, under the experimental conditions given, effects also the oxidation of the sulfur atom in the heterocyclic ring to give VIc.

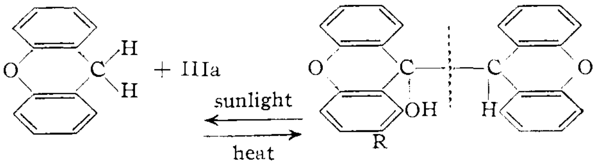
On the other hand, 2-chloro-, 4-chloro-, 2-bromo- and 4-bromoxanthones do not condense with aromatic thiols under the conditions of the experiment.



IV and V: a, A = O, R = H
b, A = O, R = Cl
c, A = S, R = H

VIa, A = O, R = H
b, A = O, R = Cl
c, A = SO₂, R = H

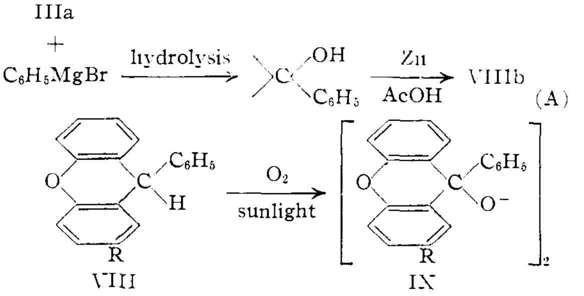
(c) **Photochemical Reactions.**[7]—In continuation of some recent work,[13] we now have found that when a benzene solution of xanthene and IIIa is exposed to sunlight in absence of air, a photoproduct VIIb separates out in crystals of great purity. This reaction is of interest from the synthetic view. At 270°, VIIb decomposes into its precursors, namely, 2-chloroxanthone (IIIa) and xanthene, showing that the ethane linkage in the carbinol is weak[14]; this is in contrast to $\alpha,\alpha,\beta,\beta$-tetraphenyl ethyl alcohol which is much more thermostable. The thermal dissociation of the carbinol VIIb may possibly be attributed to the formation of two free radicals (see broken line) which are stabilized by disproportionation.[15]



VIIa, R = H; b, R = Cl

Whereas a photochemical addition reaction takes place between xanthene and IIIa in sunlight, IIIb effects a photochemical dehydrogenation reaction,[16] yielding 9,9'-bixanthene when its benzene solution is allowed to react with xanthene in sunlight and in the absence of oxygen. The fate of the ketone has not yet been established.

9-Arylxanthenes, *e.g.*, 9-phenylxanthene (VIIIa), when their benzene solutions are exposed to sunlight in presence of air, form 9-arylxanthyl peroxides, *e.g.*, 9-phenylxanthyl peroxide (IXa).[17] We now have found that 2-chloro-9-phenylxanthene (VIIIb) behaves similarly under the action of sunlight in the presence of oxygen, yielding 2-chloro-9-phenylxanthyl peroxide (IXb). VIIIb has been synthesized as shown in scheme A.



a, R = H; b, R = Cl

The photo-peroxide formation of IX under the influence of sunlight possibly may be attributed to a direct attack by oxygen on an excited form of VIII. That IXb is a peroxide is established by the fact that it liberates iodine from potassium iodide solution in acetic acid, IXb gives IIIa on pyrolysis.

## Experimental

**Action of Lithium Aluminum Hydride on:** (a) Halogen **Substituted Xanthones IIIa-d.**—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 minutes, a benzene solution (30 ml.) containing 1 g. of each of IIIa-d was added in portions. The reaction mixture was refluxed for three hours and then kept overnight at room temperature. After treatment with cold dilute hydrochloric acid, the ethereal solutions were worked up as follows: The solid residues which were obtained after the washing with light petroleum (b.p. below 40°; *ca.* 40 ml.) were crystallized from methyl alcohol to yield xanthene in an almost quantitative yield in each case (identification was carried out by m.p. and mixed m.p.[6]).

(**b**) 1-**Chloro-4-methylxanthone** (**IVa**).—One gram of IVa was treated with lithium aluminum hydride as described above and the reaction mixture was refluxed for two hours. It was decomposed with cold saturated aqueous ammonium chloride solution (*ca.* 100 ml.), extracted with ether, dried and evaporated. The solid residue so obtained was crystallized from benzene and light petroleum as colorless crystals (*ca.* 0.73 g.), m.p. 170° (yellow melt). *Anal.* Calcd. for $C_{14}H_{11}ClO_2$: C, 68.1; H, 4.5; Cl, 14.4; active H, 0.40; mol. wt., 246. Found: C, 67.9; H, 4.4; Cl, 14.3; active H, 0.38; mol. wt., 231. 1-Chloro-4-methylxanthydrol is easily soluble in benzene and acetone, but difficultly soluble in light petroleum and cold ethyl alcohol. It gives an orange color with sulfuric acid.

**Action of Metallic Sodium and Alcohol on IIIa-d.**—A solution of 1 g. of each of IIIa-d in 25 ml. of hot absolute ethyl alcohol was added dropwise to 1 g. of molten metallic sodium after the method described by Heller and Kostan-

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[9] A. M. v. dem Knesebeck and F. Ullmann, *Ber.*, **55**, 306 (1922).

[10] H. Mauss, *Chem. Ber.*, **81**, 19 (1948).

[11] S. Archer, L. B. Rochester and M. Jackman, THIS JOURNAL, **76**, 588 (1954).

[12] S. Archer and C. M. Suter, *ibid.*, **74**, 4296 (1952).

[13] *Cf.* the photochemical addition of diarylmethanes to diarylketones, *e.g.*, xanthene to xanthone to give tetraarylethanol 9,9'-bixanthen)-9-ol (VIIa) (A. Schönberg and A. Mustafa, *J. Chem. Soc.*, 67 (1944), and *Chem. Revs.*, **40**, 181 (1947)).

[14] *Cf.* the thermal dissociation of (9,9'-bixanthen)-9-ol (VIIa) into xanthone and xanthene (A. Schönberg and A. Mustafa, *J. Chem. Soc.*, 551 (1945)).

[15] *Cf.* the photo-dissociation of 10-(9-xanthyl)-10-thiaxanthenol in sunlight to thiaxanthone and xanthene (ref. 14).

[16] *Cf.* the photochemical dehydrogenation of diphenylmethane and anthrone by xanthone to give tetraphenylethane and 10,10'-bianthrone, respectively (ref. 13).

[17] A. Schönberg and A. Mustafa, *J. Chem. Soc.*, 657 (1945); 997 (1947).

TABLE I

ARYLMERCAPTOXANTHONES AND THEIR CORRESPONDING SULFONE DERIVATIVES

| Compound | Thiol R′ | M.p.,[a] °C. | Yield, % | Formula | Carbon, % Calcd. | Carbon, % Found | Hydrogen, % Calcd. | Hydrogen, % Found | Sulfur, % Calcd. | Sulfur, % Found |
|---|---|---|---|---|---|---|---|---|---|---|
| Va | $C_6H_4CH_3$-*o* | 170 | 52 | $C_{21}H_{16}O_2S$ | 75.9 | 75.8 | 4.8 | 4.5 | 9.7 | 9.5 |
| | $C_6H_4CH_3$-*m* | 163 | 58 | | | 75.6 | | 4.7 | | 9.5 |
| | $C_6H_4CH_3$-*p* | 166 | 73 | | | 75.8 | | 4.6 | | 9.4 |
| Vb | $C_6H_5$ | 164 | 81 | $C_{20}H_{13}ClO_2S$ | 68.1 | 68.0 | 3.7 | 3.5 | 9.1 | 8.8 |
| | | | | | | | | | Cl, 10.1 | 9.9 |
| | $C_6H_4CH_3$-*o* | 205 | 62 | $C_{21}H_{15}ClO_2S$ | 68.8 | 68.8 | 4.1 | 3.9 | 8.7 | 8.5 |
| | | | | | | | | | 9.7 | 9.6 |
| | $C_6H_4CH_3$-*m* | 140 | 58 | | | 68.5 | | 4.0 | | 8.5 |
| | | | | | | | | | | 9.7 |
| | $C_6H_4CH_3$-*p* | 180 | 78 | | | 68.7 | | 3.7 | | 8.6 |
| | | | | | | | | | | 9.5 |
| Vc | $C_6H_5$ | 150 | 83 | $C_{20}H_{14}OS_2$ | 71.8 | 71.6 | 4.2 | 4.2 | 19.1 | 18.8 |
| | $C_6H_4CH_3$-*o* | 162 | 64 | $C_{21}H_{16}OS_2$ | 72.4 | 72.4 | 4.6 | 4.3 | 18.4 | 18.1 |
| | $C_6H_4CH_3$-*m* | 140 | 61 | | | 72.1 | | 4.5 | | 18.3 |
| | $C_6H_4CH_3$-*p* | 164 | 84 | | | 72.1 | | 4.6 | | 18.4 |
| VIa | $C_6H_4CH_3$-*o* | 260 | 63 | $C_{21}H_{16}O_4S$ | 69.1 | 68.9 | 4.4 | 4.4 | 8.8 | 8.6 |
| | $C_6H_4CH_3$-*m* | 226 | 61 | | | 68.9 | | 4.3 | | 8.7 |
| | $C_6H_4CH_3$-*p* | 270 | 76 | | | 69.0 | | 4.4 | | 8.5 |
| VIb | $C_6H_5$ | 210–212 | 84 | $C_{20}H_{13}ClO_4S$ | 62.4 | 62.1 | 3.4 | 3.3 | 8.3 | 8.2 |
| | | | | | | | | | 9.2 | 9.1[b] |
| | $C_6H_4CH_3$-*o* | 242 | 73 | $C_{21}H_{15}ClO_4S$ | 63.2 | 62.9 | 3.8 | 3.7 | 8.1 | 7.8 |
| | | | | | | | | | 8.9[b] | 8.7[b] |
| | $C_6H_4CH_3$-*m* | 198 | 69 | | | 63.1 | | 3.5 | | 8.0 |
| | | | | | | | | | | 8.5[b] |
| | $C_6H_4CH_3$-*p* | 240 | 79 | | | 62.9 | | 3.6 | | 7.9 |
| | | | | | | | | | | 8.8 |
| VIc | $C_6H_5$ | 176 | 82 | $C_{20}H_{14}O_5S_2$ | 60.0 | 59.9 | 3.5 | 3.3 | 16.1 | 16.0 |
| | $C_6H_4CH_3$-*o* | 180 | 75 | $C_{21}H_{16}O_5S_2$ | 61.1 | 60.8 | 3.9 | 3.7 | 15.6 | 15.5 |
| | $C_6H_4CH_3$-*m* | 182 | 70 | | | 61.0 | | 3.7 | | 15.3 |
| | $C_6H_4CH_3$-*p* | 210 | 85 | | | 60.9 | | 3.5 | | 15.5 |

[a] Melting points are uncorrected.

ecki.[6] The reaction mixture was steam distilled and the solid, so obtained, was crystallized from methyl alcohol, m.p. 101°, identified as xanthene (m.p. and mixed m.p.); yield is almost quantitative in each case.

**Action of Aromatic Thiols. General Procedure.**—A solution of 2 g. of each of IVa-c and 1.5 g. of thiol in 25 ml, of amyl alcohol was treated with 0.1 g. of solid potassium hydroxide. The reaction mixture was refluxed for three hours and kept overnight at room temperature. The yellow solid that separated was filtered off, 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 arylmercapto derivatives Va-c (*cf*, Table I) form yellow crystals which are easily soluble in benzene and chloroform, but difficultly soluble in cold ethyl alcohol and petroleum ether. They give orange-red color with sulfuric acid.

Va-c were oxidized to the corresponding sulfones (VIa-c) (*cf.* Table I) as follows: 1 g. of each of Va-c was dissolved in 25 ml. of glacial acetic acid and then treated with 5 ml. of hydrogen peroxide (30%). The reaction mixture was heated (steam-bath) for one hour and kept aside overnight at room temperature. The resulting solid was crystallized from glacial acetic acid.

The sulfones VIa-c are colorless, easily soluble in hot xylene, but 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 (Kahlbaum) and dried over sodium. The reaction mixture was placed in a Schlenk tube[18] of Pyrex glass, and the air then was displaced by dry carbon dioxide and the tube sealed by fusion.

The photo-formation 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) **Xanthene and IIIa.**—A solution of 1 g. of xanthene and 1.3 g. of IIIa in 30 ml. of benzene, after being exposed to sunlight for 10 days (May), acquired a green fluorescence, and the photo-product separated out during exposure as colorless needles. These were collected, washed with cold benzene (*ca.* 10 ml.) and recrystallized from hot benzene. The yield of VIIb is *ca.* 80% and melts at 174° dec. *Anal.* Calcd. for $C_{26}H_{17}ClO_3$: C, 75.7; H, 4.1; Cl, 8.5, Found: C, 75.6; H, 3.9; Cl, 8.4. It dissolves with difficulty in concentrated sulfuric acid giving an orange solution.

(b) **Xanthene and IIIb.**—The above experiment was repeated, using a mixture of 0.7 g, of IIIb and 0.5 g. of xanthene dissolved in 25 ml, of benzene. The reaction mixture was exposed to sunlight for 10 days (July); the solution acquired green fluorescence after one-day exposure. The oily residue, so obtained after removal of benzene in a vacuum, formed a semi-solid mass on cooling. It was washed with light petroleum (b.p. 50–60°, *ca.* 25 ml.) and crystallized from benzene as colorless crystals (*ca.* 0.32 g.), m.p. 201°, identified as 9,9′-bixanthene (m.p. and mixed m.p.). *Anal.* Calcd. for $C_{26}H_{18}O_2$: C, 86.2; H, 4.97. Found: C, 86.1; H, 5.0.

(c) **VIIIb and Oxygen.**—To a Grignard solution (prepared from 0.9 g. of magnesium and 9 g. of bromobenzene in 50 ml. of dry ether) was added a solution of 1 g. of IIIa in 50 ml, of dry benzene. After evaporation of the ether, the mixture was heated for one hour on a steam-bath. After standing overnight at 25°, it was poured slowly into 100 ml. of saturated aqueous ammonium chloride solution and the ether was dried ($Na_2SO_4$), filtered and evaporated. The oily residue was washed with light petroleum (below 40°, *ca.* 35 ml.) and the resulting solid crystallized from petroleum ether (b.p. 60–80°) as colorless crystals (*ca.* 0.87 g.), m.p. 113°. *Anal.* Calcd. for $C_{19}H_{13}ClO_2$: C, 74,0; H, 4.2; Cl, 11.4; active H, 0.32. Found: C, 73.8; H,

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

4.0; Cl, 11.3; active H, 0.30. 9-Phenyl-2-chloroxanthydrol is easily soluble in cold benzene, ether and hot ethyl alcohol and gives an orange color with sulfuric acid.

Reduction of 9-phenyl-2-chloroxanthydrol was carried out as described by Ullmann and Engi[19] for phenylxanthene (VIIIa), *i.e.*, by means of zinc dust and acetic acid with platinum chloride as a catalyst. VIIIb was crystallized from ethyl alcohol as colorless crystals, m.p. 139°, in almost quantitative yield. *Anal.* Calcd. for $C_{19}H_{13}ClO$: C, 78.1; H, 4.5; Cl, 11.98. Found: C, 77.9; H, 4.4; Cl, 12.0. It is easily soluble in benzene, but sparingly soluble in cold ethyl alcohol and gives no color with sulfuric acid.

A solution of 1 g. of VIIIb was exposed to sunlight for 15 days (April). The colorless crystals that separated out during exposure were recrystallized from benzene (*ca.* 0.63 g.), m.p. 221° dec., brown-red melt. *Anal.* Calcd. for $C_{38}H_{24}Cl_2O_4$: C, 74.3; H, 3.9; Cl, 11.4. Found: C, 74.1; H, 3.8; Cl, 11.3. IXb is soluble in hot benzene and xylene, but difficultly soluble in ethyl alcohol and gives an orange-yellow color with sulfuric acid.

Thermal decomposition of 0.5 g. of IXb for half an hour at 270° (bath-temp.) afforded xanthone (*ca.* 0.18 g.) (m.p. and mixed m.p. and color reaction with sulfuric acid) as a pale-yellow sublimate.

GIZA, CAIRO, EGYPT

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[19] F. Ullmann and E. Engi, *Ber.*, **37**, 2371 (1904).

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

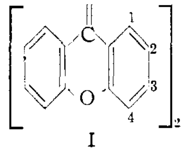
# Thermochromism of Dixanthylenes. II[1]

BY AHMED MUSTAFA AND MOHAMED EZZ EL-DIN SOBHY

RECEIVED APRIL 12, 1955

Substitution in dixanthylene (I) in positions 1 and 1′, which hinders the planarity of the whole molecule, is detrimental to the development of thermochromic properties (Table I). Fission of the central ethylene linkage in dixanthylenes Ia-d is brought about by the action of thionyl chloride followed by water to give the corresponding xanthone derivatives and by the action of sulfur at 270° to yield the corresponding xanthione derivatives. Three new xanthone derivatives Va-c, needed in this investigation, have been synthesized.

In continuation of the study of constitutional changes in thermochromic substances leading to non-thermochromic substances,[2] we now have extended our previous investigation[1] to show how substitution affects the thermochromic properties of dixanthylene (I); a strongly thermochromic substance, the crystals are colorless in liquid air, blue-greenish on heating and the melt is deep blue-green.[3] The results are shown in Table I; the substances were tested in boiling diphenyl ether solutions.



I

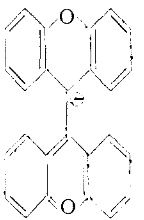
TABLE I

| | |
|---|---|
| 2,2′-Dibromo- (Ia) | Strongly thermochromic |
| 4,4′-Dibromo- (Ib) | Strongly thermochromic |
| 2,3,2′,3′-Tetramethyl- (Ic) | Strongly thermochromic |
| 2,4,2′,4′-Tetramethyl- (Id) | Strongly thermochromic |
| 1,4,1′,4′-Tetramethyl- (Ie) | Not thermochromic |
| 1,3,1′,3′-Tetramethyl- (If) | Not thermochromic |

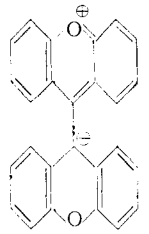
## Discussion of the Results

Recently, Schönberg, Mustafa and Asker[2] advanced a hypothesis that "in overcrowded molecules in which planarity is hindered, the degree of non-planarity changes with temperature. This is associated with change of color, one reason being that resonance is related to planarity." Dixanthylenes, *e.g.*, I, a thermochromic compound, lose this property upon substitution at positions 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 temperatures. From this, it has been concluded that the green forms of I and its analogs, the "colored molecules" have a greater degree of planarity; the experiments of thermochromic bianthrones have led Hirshberg, Loewenthal, Bergmann and Pullman[4] to similar conclusions.

**Action of Thionyl Chloride on Dixanthylenes.** Dixanthylene shows remarkable behavior toward thionyl chloride, followed by the action of water.[5] Fission of the central ethylene bond, which has single bond character (*cf.* IIa and IIb), occurs and xanthone is formed. The authors have now found that Ia-d behaved analogously, yielding 2-bromo-, 4-bromo-, 2,3-dimethyl- (Vc) and 2,4-dimethylxanthones (Vd), respectively.

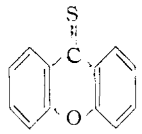


IIa



IIb

**Action of Sulfur on Dixanthylenes.**—Fission of the central ethylene linkage in dixanthylenes Ia-d is brought about by the action of sulfur[6] at 270° for a few minutes, with the formation of the corresponding xanthones III.



III

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[1] For part I *cf.* A. Schönberg, A. Mustafa and M. E. E. Sobhy, THIS JOURNAL, **75**, 3377 (1953).

[2] A. Schönberg, A. Mustafa and W. Asker, *ibid.*, **76**, 4134 (1954).

[3] A. Schönberg and O. Schütz, *Ber.*, **61**, 478 (1928).

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

[5] A. Schönberg and W. Asker, *J. Chem. Soc.*, 725 (1942).

[6] A. Schönberg, A. Ismail and W. Asker, *ibid.*, 442 (1946).