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# DIBENZOXANTHYLIUM SALTS—III*

## STUDIES ON 9-METHYLENE-3,4,5,6-DIBENZOXANTHENE AND 3,4,5,6-DIBENZOXANTHYLOMETHINES

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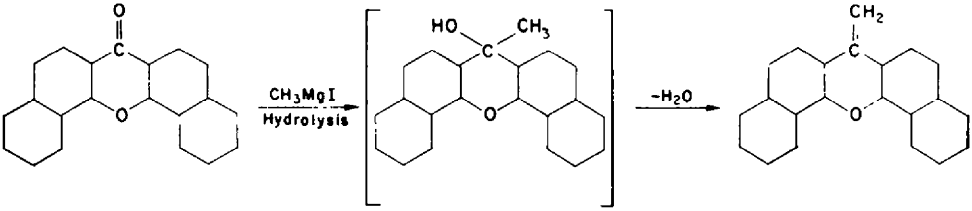
**Abstract**—Synthesis and reactions of 9-methylene-3,4,5,6-dibenzoxanthene (III) are described. Starting from 9-methyldibenzoxanthylium perchlorate (V) several new dibenzoxanthylocyanine dyes are obtained by classical methods. For the preparation of ω-aldehyde (IX) an easy method is reported. A number of 3,4,5,6-dibenzoxanthylomerocyanine dyes (XIV) have been prepared by the condensation of IX with active methylene compounds. Several interesting relations between the constitution and colour of the synthesized dyes have been revealed.

IN PARTS I and II of this series the relations between the constitution and colour of several 3,4,5,6-dibenzoxanthylium compounds have been investigated. In the present communication a report on the synthesis and reactions of 9-methylene-3,4,5,6-dibenzoxanthene (III) and 3,4,5,6-dibenzoxanthylocyanine dyes is given. Furthermore, the preparation of 9-methylene-3,4,5,6-dibenzoxanthene-ω-aldehyde (IX) and several merocyanine dyes obtained by the condensation of the latter with active methylene compounds is included.

9-Methylene-3,4,5,6-dibenzoxanthene (III) can be readily obtained by treating 3,4,5,6-dibenzoxanthone (I) with an excess of methylmagnesium iodide, followed by hydrolysis. The intermediate dibenzoxanthenol (II) could not be isolated. The direct formation of III from I as pointed out above may be compared with the formation of 9-benzylidene-1,2,7,8-dibenzoxanthene by the action of benzylmagnesium chloride on 1,2,7,8-dibenzoxanthone.[1]



I II III

The structure of the methylene derivative (III) was inferred from the fact that it gives correct analytical figures and undergoes all reactions typical of analogously constituted compounds.[2,3]

When a suspension of III in glacical acetic acid was treated with perchloric acid,

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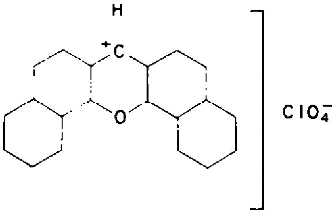
* Part I, M. Kamel, *Helv. Chim. Acta*, **42**, 580 (1959).
Part II, M. Kamel and R. Wizinger, *Helv. Chim. Acta* **43**, 594 (1960).

[1] W. Dilthey and H. Giebert, *Ber. Dtsch. Chem. Ges.* **76B**, 1084 (1943).

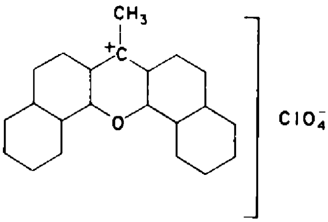
[2] R. Wizinger, *J. Prak. Chem.* **154**, 1 (1939).

[3] Y. Al-Attar, Ph.D. Thesis, Univ. Zurich (1946).

9-methyl-3,4,5,6-dibenzoxanthylium perchlorate (V) was formed. A solution of V in glacial acetic acid is orange in colour and shows a sharp absorption band in the violet and blue regions of the spectrum ($\lambda_{max}$ 464 m$\mu$).



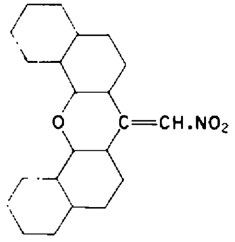
IV*; orange, $\lambda_{max}$ 470 m$\mu$



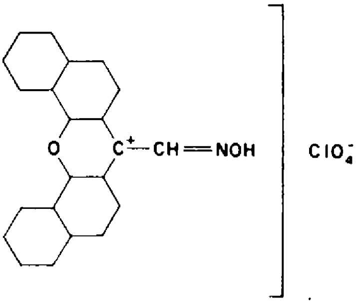
V*; orange, $\lambda_{max}$ 464 m$\mu$

It has already been shown, in part I, that 3,4,5,6-dibenzoxanthylium perchlorate shows a maximum absorption at 470 m$\mu$. The replacement of the hydrogen atom in position 9 of IV by a methyl group causes, therefore, a hypsochromic shift of 6 m$\mu$. In this connection, it may be pointed out that the introduction of a phenyl group in the same position causes a bathochromic shift of 8 m$\mu$ (cf. part I).

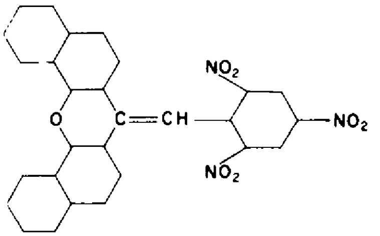
Furthermore, it was also found that the reactions of III with tetranitromethane, nitrous acid and picryl chloride proceeded in an analogous manner to the reactions of 9-methylene-1,2,7,8-dibenzoxanthene with these reagents.[2,3] Nitration of III proceeded smoothly when tetranitromethane was used as nitrating agent, giving compound VI. Amyl nitrite and hydrochloric acid (nitrous acid) caused nitrosation and the nitroso compound was isolated in the form of the perchlorate derivative (VII; oxime form). Picryl chloride reacted with III readily yielding VIII.



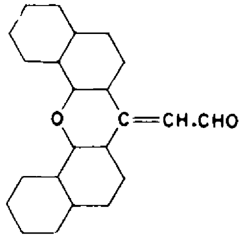
VI; yellow, $\lambda_{max}$ 424 m$\mu$
(in acetic acid)



VII; red, $\lambda_{max}$ 498 m$\mu$
(in acetic acid)



VIII; orange red, $\lambda_{max}$ 489 m$\mu$
(in acetic acid)



IX; yellow, $\lambda_{max}$ 396 m$\mu$
(in benzene)

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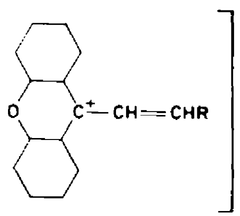
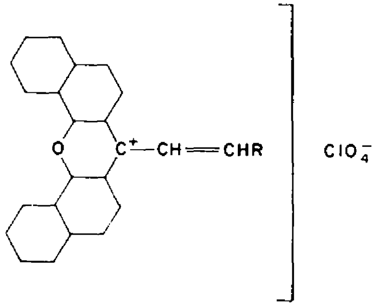
* Carbonium ion structures are used throughout in favour of simplification and better representation of the reactions involved.

It is known that an aldehyde group can be introduced by the treatment of the appropriate heterocyclic compound having a reactive methyl or methylene group with formylating agents.[4] Starting from III, it is now possible using Vilsmeyer aldehyde synthesis[2] to prepare 9-methylene-3,4,5,6-dibenzoxanthene-$\omega$-aldehyde (IX). The formation of the latter compound proceeds in an analogous manner to the formation of 9-methylene-$\omega$-aldehyde.[5]

Styrylxanthylium salts of the general type (X) have been previously prepared by several investigators.[6–8] Analogous compounds containing the dibenzoxanthylium moiety are as yet unknown. The synthesis of the three compounds (XIa–c) could be easily effected by condensing V with *p*-dimethylaminobenzaldehyde, *p*-dimethylaminocinnamaldehyde and *p*-methoxybenzaldehyde, respectively. It may be pointed out in this connection that the vinylene shift in the wave lengths of maximum absorption between XIa and XIb amounts to 89 mμ, i.e. less than the normal shift by 11 mμ.[9]

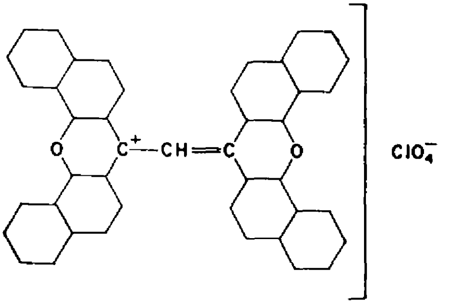


X

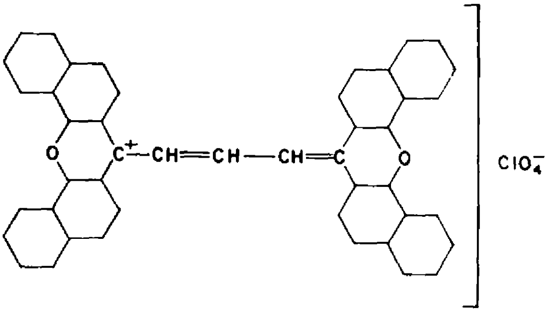


XI; a, R = $—C_6H_4·N(CH_3)_2$
b, R = $—CH═CH—C_6H_4·N(CH_3)_2$
c, R = $—C_6H_4·OCH_3(p)$.

Starting from the same perchlorate (V), it is now possible to prepare the symmetrical 3,4,5,6-dibenzoxanthylocyanines (XII and XIII), respectively.



XII; blue green, $\lambda_{max}$ 680 mμ
(in chloroform)



XIII; green, $\lambda_{max}$ 756 mμ
(in nitromethane)

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[4] K. Venkataraman, *The Chemistry of Synthetic Dyes*, Vol. II, p. 1157. Academic Press, New York (1952).

[5] R. Wizinger and U. Arni, *Ber. Dtsch. Chem. Ges.* **92**, 2309 (1959).

[6] K. Ziegler and C. Ochs, *Ber. Dtsch. Chem. Ges.* **55**, 2257 (1922).

[7] H. Atkinson and I. M. Heilbron, *J. Chem. Soc.* 67 (1926).

[8] R. Wizinger and G. Renckhoff, *Helv. Chim. Acta* **24**, 369E (1941).

[9] H. Schmidt and R. Wizinger, *Liebigs Ann.* **623**, 204 (1959).

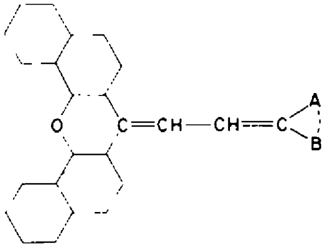
The monomethine dye (XII) was obtained by two methods: (a) direct condensation of V with I and (b) condensation of V with IV.

It is noteworthy to mention that the condensation in the first case proceeds without the addition of a mixture of phosphorous oxychloride and pentachloride.[8]

Trials to prepare the trimethine dye (XIII) by condensing V with ethylorthoformate were unsuccessful. However, XIII was readily obtained when V was condensed with the ω-aldehyde (IX).

The vinylene shift between compound XII and XIII was found to amount to 76 mμ, i.e. less than the normal vinylene shift by 24 mμ. Similar deviations have been observed also by many other investigators.[10,11]

Finally, some 3,4,5,6-dibenzoxanthylomerocyanine dyes of the general type (XIV) were synthesized by condensation of IX with active methylene compounds.



XIV

Table 1 contains a list of the active methylene compounds used and the wavelengths of maximum absorption of the dyes synthesized.

TABLE 1

| Merocyanine | Active methylene compounds | Colour of soln | $\lambda_{max}$ (mμ) in acetic acid |
|---|---|---|---|
| (XV) | Acetylacetone | yellow | 410 |
| (XVI) | 1-Phenyl-3-methylpyrazolone | orange | 490 |
| (XVII) | Barbituric acid | orange | 442, 551 |
| (XVIII) | Cyanoacetic ester | orange | 460 |
| (XIX) | Malononitrile | orange | 480 |
| (XX) | 3-Hydroxythionaphthene | red | 525 |

## EXPERIMENTAL*

*9-Methylene-*3,4,5,6-*dibenzoxanthene* (III)

To a Grignard solution (prepared from 0·9 g Mg, 7 g methylmagnesium iodide and 50 ml dry ether) was added a solution of 1 g 3,4,5,6-dibenzoxanthone (I) in dry benzene (50 ml). The water was removed from the reflux condenser and the ether was evaporated from the reaction mixture which then was heated for 3 hr on a steam-bath. After the mixture had stood overnight at 25°, it was poured slowly into 50 ml saturated $NH_4Cl$ aq., and the reaction mixture extracted with ether. The ether–benzene mixture was dried ($Na_2SO_4$) evaporated and the product crystallized from benzene in colourless crystals (or faintly pink coloured), m.p. 181°, yield ca. 50%. (Found: C, 89·8; H, 4·8. $C_{22}H_{14}O$ requires: C, 89·8; H, 4·8%).

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* The wavelengths of maximum absorption are reported under the corresponding formulae in the Introduction except for XIa–c.

[10] K. J. Brunnings and A. H. Corwin, *J. Amer. Chem. Soc.* **64**, 593 (1942).

[11] L. G. S. Brooker, F. L. White, R. H. Sprague, S. G. Dent, Jr, and G. Van Zandt, *Chem. Rev.* **41**, 325 (1947).

The methylene derivative (III) is sparingly soluble in pet. ether (70/80°) but readily soluble in alcohol, benzene or chloroform giving colourless solutions. It dissolves in conc $H_2SO_4$ with an orange colour which shows green fluorescence.

### 9-*Methylene*-3,4,5,6-*dibenzoxanthylium perchlorate* (V)

To a solution of perchloric acid (2 ml, 70%) in glacial acetic acid (10 ml), 1 g III was added. The mixture was heated on a steam-bath for few min and then left for 1 hr at room temp. At the end of this period, the orange crystals that formed were filtered off and crystallized from nitromethane; orange prisms, m.p. 263–264° (dec.) yield almost quantitative. (Found: C, 66·7; H, 3·9; Cl, 8·7. $C_{22}H_{15}O_5Cl$ requires: C, 66·9; H, 3·8; Cl, 9·0%).

The perchlorate (V) is sparingly soluble in pet. ether (70/80°), benzene and chloroform but soluble in glacial acetic acid, acetic anhydride and nitromethane giving orange solutions. It gives an orange colour with conc $H_2SO_4$. Its colour disappears on boiling with pyridine.

### 9-*Nitromethylene*-3,4,5,6-*dibenzoxanthene* (VI)

A solution of III (1 g) in pyridine (10 ml) was cooled in ice and then treated dropwise with a solution of tetranitromethane (0·75 g) in the same solvent. The yellow product that separated on standing was filtered off and crystallized from nitromethane, yellow crystals, m.p. 216°, yield 73%. (Found: C, 77·7; H, 3·7; N, 4·1. $C_{22}H_{13}O_3N$ requires: C, 77·9; H, 3·9; N, 4·1%).

Compound VI is sparingly soluble in pet. ether, benzene and alcohol but soluble in acetic acid, acetic anhydride, pyridine and nitromethane with a yellow colour. It gives a red colour with conc $H_2SO_4$.

### 9-*Formaldoximo*-3,4,5,6-*dibenzoxanthylium perchlorate* (VII)

To a suspension of III (1 g) in glacial acetic acid (30 ml), amyl nitrite (10 drops) was added gradually with stirring. The reaction mixture was left for 1 hr at room temp and then treated with conc HCl (2 ml). The red coloured solution thus obtained was then treated with perchloric acid (1 ml, 70%) and the reaction mixture was left overnight in an ice-chest. The dark red crystalline product that separated was filtered off and washed with a little alcohol and ether, m.p. 316° (dec), yield 90%. (Found: C, 62·0; H, 3·5; N, 3·1; Cl, 8·1. $C_{22}H_{14}ClNO_6$ requires: C, 62·3; H, 3·3; N, 3·3; Cl, 8·4%).

Compound VII is sparingly soluble in pet. ether, benzene, alcohol and acetic acid. It dissolves in nitromethane with a red colour. It gives a red colour with conc $H_2SO_4$.

### 9-(2′,4′,6′-*Trinitrophenyl*)*methylene*-3,4,5,6-*dibenzoxanthene* (VIII)

A mixture of III (0·73 g) and picryl chloride (0·6 g) in dry benzene was refluxed 3 hr (steam-bath). After cooling the precipitated dark crystals were filtered off and washed with dry benzene. Recrystallization from nitromethane gave dark brown crystals, m.p. 199° (dec), yield 83%. (Found: C, 66·4; H, 3·0; N, 8·3. $C_{28}H_{15}N_3O_7$ requires: C, 66·5; H, 3·0; N, 8·3%). Compound VIII is sparingly soluble in pet. ether, alcohol and acetic acid but dissolves in benzene, nitromethane and nitrobenzene giving red solutions. It gives a brownish red colour with conc $H_2SO_4$.

### 9-*Methylene*-3,4,5,6-*dibenzoxanthene-ω-aldehyde* (IX)

N-Formyl-aniline (2·8 g) was added dropwise during 30 min to phosphorus oxychloride (10 g). To this mixture 6 g III was gradually added with stirring. The mixture was left for 5 hr at room temp. It was then poured into ice-water and the red brown viscous mass thus formed was separated by decantation, neutralized ($Na_2CO_3$ aq.) and finally washed with water. It was then dissolved in alcohol and hydrolysed with alcoholic NaOH (10%). On cooling the ω-aldehyde was obtained as a yellow precipitate. It was recrystallized from benzene in the form of yellow needles, m.p. 205°, yield ca. 40%. (Found: C, 85·6; H, 4·4. $C_{22}H_{14}O_2$ requires: C, 85·7; H, 4·4%).

The ω-aldehyde (IX) is sparingly soluble in pet. ether but readily soluble in alcohol, benzene and chloroform. It gives an orange red colour with conc $H_2SO_4$.

### 9-(4′-*Dimethylaminostyryl*)-3,4,5,6-*dibenzoxanthylium perchlorate* (XIa)

A mixture of perchlorate (V; 0·3945 g) and *p*-dimethylaminobenzaldehyde (0·149 g) in acetic anhydride (10 ml) was heated under reflux for 30 min. After cooling, the bronzy green crystals that formed were filtered off and recrystallized from acetic anhydride, m.p. 226° (dec.), yield almost quantitative. (Found: C, 70·5; H, 4·5; N, 2·7; Cl, 6·8. $C_{31}H_{24}ClNO_6$ requires: C, 70·8; H, 4·6; N, 2·7; Cl, 6·7%).

Compound XIa is sparingly soluble in benzene and alcohol. It dissolves in nitromethane and acetone with a green colour. It gives a red colour with conc $H_2SO_4$. Boiling with pyridine causes decolourization. $\lambda_{max}$ in nitromethane, 706 mμ.

### 9-(4′-*Dimethylaminocinnamylidene)methyl*-3,4,5,6-*dibenzoxanthylium perchlorate* (XIb)

Similarly prepared from V (1/1000 mole) and *p*-dimethylaminocinnamaldehyde (1/1000 mole). Recrystallization from nitromethane gave green crystals, m.p. 230° (dec.), yield almost quantitative. (Found: C, 72·0; H, 4·5; N, 2·4; Cl, 6·6. $C_{33}H_{26}ClNO_6$ requires: C, 71·8; H, 4·7; N, 2·5; Cl, 6·4%).

Compound XIb is sparingly soluble in benzene and alcohol. It is soluble in nitromethane and acetone with a green colour. It gives a red colour with conc $H_2SO_4$. When it is heated with pyridine the colour fades to yellow, $\lambda_{max}$ in nitromethane, 795 mμ.

### 9-(4′-*Methoxystyryl*)-3,4,5,6-*dibenzoxanthylium perchlorate* (XIc)

To a saturated solution of dry hydrogen chloride gas in a mixture of acetic acid and acetic anhydride (20:5 ml), the ethylene (III; 1·47 g) and *p*-methoxybenzaldehyde (0·68 g) was added. The mixture was heated for 1 hr. On cooling, dark violet crystals of the chloride separated. The chloride was transformed to the perchlorate by dissolution in acetic acid and addition of perchloric acid. Recrystallization from nitromethane gave violet prisms, m.p. 262° (dec.), yield ca. 60%. (Found: C, 70·5; H, 4·2; Cl, 7·1. $C_{30}H_{21}ClO_6$ requires: C, 70·2; H, 4·1; Cl, 6·9%).

Compound XIc is sparingly soluble in pet. ether and benzene but dissolves readily in acetic anhydride and nitromethane giving a purple solution, $\lambda_{max}$ in acetic anhydride, 472 and 556 mμ.

### *Bis*-3,4,5,6-*dibenzoxanthene-monomethine perchlorate* (XII)

(a) A solution of perchlorate (V; 0·3945 g) in nitromethane (10 ml) was added dropwise to a boiling solution of 3,4,5,6-dibenzoxanthone (0·296 g) in a mixture of glacial acetic acid and acetic anhydride (20:10 ml) and the boiling was continued for 30 min. On cooling green crystals separated. Recrystallization from nitromethane gave bronzy green needles, m.p. 322° (dec.), yield almost quantitative. (Found: C, 76·5; H, 3·9; Cl, 5·5. $C_{43}H_{25}ClO_6$ requires: C, 76·7; H, 3·7; Cl, 5·3%).

Compound XII is sparingly soluble in common organic solvents. It dissolves in nitromethane, chloroform and acetone with a green colour. It gives an orange colour with conc $H_2SO_4$ (addition of acid). Its colour disappears on boiling with pyridine.

(b) The same product was obtained when the perchlorate (V; 1/1000 mole) was condensed with 3,4,5,6-dibenzoxanthylium perchlorate (1/500 mole) in a mixture of acetic acid and acetic anhydride as described under (a).

### *Bis*-3,4,5,6-*dibenzoxanthene-trimethine perchlorate* (XIII)

A mixture of perchlorate (V; 0·789 g), ω-aldehyde (IX; 0·322 g) and acetic anhydride (15 ml) was heated for 20 min. The product was crystallized from nitromethane as bronzy green needles, m.p. above 350°, yield almost quantitative. (Found: C, 77·2; H, 4·0; Cl, 5·3. $C_{45}H_{27}ClO_6$ requires: C, 77·3; H, 3·9; Cl, 5·1%).

Compound XIII is very sparingly soluble in common organic solvents. It dissolves in acetic anhydride and nitromethane with a green colour. It gives an orange red colour with conc $H_2SO_4$.

### [3,4,5,6-*Dibenzoxanthene*-(9)]-[*acetylacetone*]-*dimethinmerocyanine* (XV)

A solution of ω-aldehyde (IX; 0·32 g) and acetylacetone (0·1 g) in 15 ml pyridine was heated for 15 min. The condensation product was precipitated with water and filtered off, yellow needles from alcohol, m.p. 155°, yield 80%. (Found: C, 83·6; H, 4·9. $C_{28}H_{20}O_3$ requires: C, 83·2; H, 4·7%)

Compound XV is sparingly soluble in pet. ether but dissolves in benzene, alcohol and acetic acid with yellow colour. It gives a brown colour with conc $H_2SO_4$.

[3,4,5,6-*Dibenzoxanthene*-(9)]-[1-*phenyl-3-methyl-5-pyrazolone*]-*dimethinmerocyanine* (XVI)

From 0·32 g IX and 0·18 g 1-phenyl-3-methyl-5-pyrazolone in pyridine (15 ml). Recrystallization from benzene gave dark brown crystals, m.p. 298°. (Found: C, 82·7; H, 4·7; N, 5·5. $C_{33}H_{22}N_2O_2$ requires: C, 82·8; H, 4·6; N, 5·8%). Compound XVI is sparingly soluble in pet. ether and alcohol but readily soluble in benzene and acetic acid giving a red colour. It gives an orange colour with conc $H_2SO_4$.

[3,4,5,6-*Dibenzoxanthene*-(9)]-[*barbituric acid*]-*dimethinmerocyanine* (XVII)

From 0·32 g IX and 0·13 g barbituric acid brown crystals from acetic acid, m.p. above 360°. (Found: C, 74·8; H, 3·9; N, 6·6. $C_{27}H_{16}N_2O_4$ requires: C, 75·0; H, 4·0; N, 6·5%). Compound, XVII is sparingly soluble in pet. ether, benzene and alcohol. It dissolves in acetic acid giving a blue red colour. It gives an orange colour with conc $H_2SO_4$.

[3,4,5,6-*Dibenzoxanthene*-(9)]-[*cyanoacetic ester*]-*dimethinmerocyanine* (XVIII)

From 0·32 g IX and 0·11 g cyanoacetic ester; red crystals from benzene, m.p. 206°. (Found: C, 80·2; H, 4·6; N, 3·3. $C_{28}H_{19}NO_3$ requires: C, 80·6; H, 4·5; N, 3·4%). Compound XVIII is sparingly soluble in pet. ether and alcohol but dissolves in benzene and acetic acid with orange colour. It gives an orange red colour with conc $H_2SO_4$.

[3,4,5,6-*Dibenzoxanthene*-(9)]-[*malononitrile*]-*dimethinmerocyanine* (XIX)

Prepared from 0·32 g IX and 0·07 g malononitrile; red crystals from benzene, m.p. cinters at 290° and melts at 304°. (Found: C, 84·5; H, 3·9; N, 7·4. $C_{26}H_{14}NO_2$ requires: C, 84·2; H, 3·8; N, 7·6%). Compound XIX is sparingly soluble in pet. ether and alcohol, but dissolves in benzene and acetic acid giving orange solutions. It gives an orange red colour with conc $H_2SO_4$.

[3,4,5,6-*Dibenzoxanthene*-(9)]-[3-*hydroxythionaphthene*]-*dimethinmerocyanine* (XX)

From 0·32 g IX and 0·15 g 3-hydroxythionaphthene: dark red crystals from benzene, m.p. 238°. (Found: C, 81·5; H, 4·2; S, 6·8. $C_{31}H_{18}O_2S$ requires: C, 81·9; H, 4·0; S, 7·0%). Compound XX is sparingly soluble in pet. ether and alcohol, but soluble in benzene and acetic acid. It gives a red colour with conc $H_2SO_4$.

*Acknowledgement*—The authors are greatly indebted to Professor Dr. Robert Wizinger, Head of the Institute of Dyestuff Chemistry, Basle, Switzerland for his interest in the present investigation.