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DIBENZOXANTHYLIUM SALTS—IV

STUDIES ON 1,2,5,6-DIBENZO- AND 2,3,5,6-DIBENZOXANTHYLIUM COMPOUNDS

M. Kamel and H. Shoeb
The Dyeing and Textile Finishing Unit, Textile Research Centre, Dokki,
Cairo, U.A.R.

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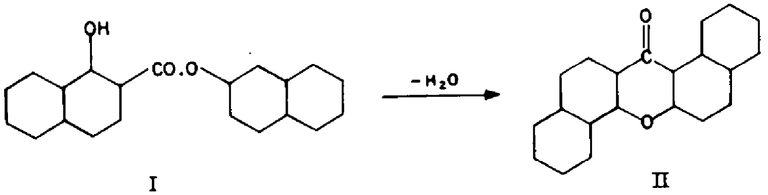
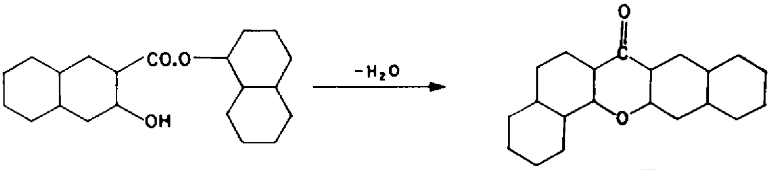
Abstract—A novel synthesis of the hitherto unknown 1,2,5,6-dibenzoxanthone (II) and 2,3,5,6-dibenzoxanthone (IV) has been successfully achieved. Reactions of these two compounds are described. Study on the relation between the constitution and colour in 1,2,5,6-dibenzo- and 2,3,5,6-dibenzoxanthylium compounds is included.

In parts I, II and III* of this series a study of the synthesis and properties of several new 3,4,5,6-dibenzoxanthylium compounds has been carried out. In the present communication, the synthesis of the hitherto unknown 1,2,5,6-dibenzoxanthone (II) and 2,3,5,6-dibenzoxanthone (IV) and several of their derivatives including the corresponding dibenzoxanthylium salts is described. Furthermore, the effect of annelation on the colour in the two new series of dibenzoxanthylium compounds has been revealed.

The preparation of the two new dibenzoxanthones was successfully carried out by heating 1-hydroxy-2-(2′-naphthyl)naphthoate (I) and 3-hydroxy-2-(1′-naphthyl)-naphthoate (III) at 300–325° for 45–60 minutes. The formation of II and IV from I and III follows the rules of Strohbach on the pyrolysis of *o*-hydroxyaryl esters.[1]



I II



III IV

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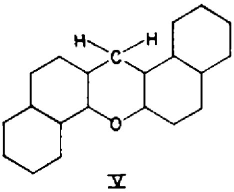
* Part I, M. Kamel, *Helv. Chim. Acta*, **42**, 580 (1959).
Part II, M. Kamel and R. Wizinger, *Helv. Chim. Acta*, **43**, 594 (1960).
Part III, Preceding paper.

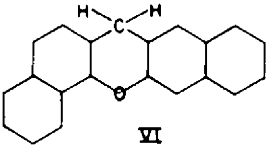
[1] E. Strohbach, *Ber. Dtsch. Chem. Ges.* **34**, 4136 (1901).

The elucidation of the structures II and IV is based on the following facts: (a) they give correct analytical figures; (b) they give no colour with alcoholic ferric chloride solution; (c) they do not dissolve in aqueous sodium hydroxide solution; (d) they are not identical with 3,4,5,6-debenzoxanthone and 1,2,6,7-dibenzoxanthone; and (e) they undergo all typical reactions of xanthones and dibenzoxanthones.

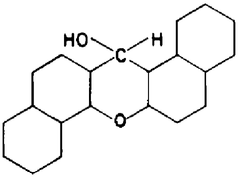
Compounds II and IV are reduced by lithium aluminium hydride to 1,2,5,6-dibenzoxanthene (V) and 2,3,5,6-dibenzoxanthene (VI) respectively. However, reduction with sodium amalgam in ethyl acetate gave 1,2,5,6-dibenzoxanthenol (VII) and 2,3,5,6-dibenzoxanthenol (VIII).



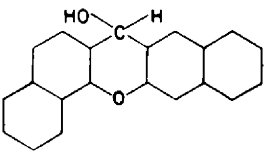
V



VI

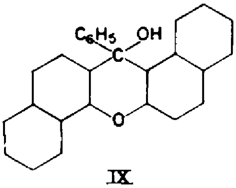


VII

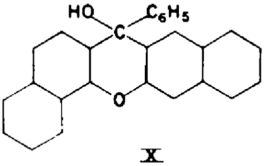


VIII

When II and IV are treated with an excess of phenylmagnesium bromide, and the product hydrolysed, 9-phenyl-1,2,5,6-dibenzoxanthenol (IX) and 9-phenyl-2,3,5,6-dibenzoxanthenol (X) are formed in good yields.

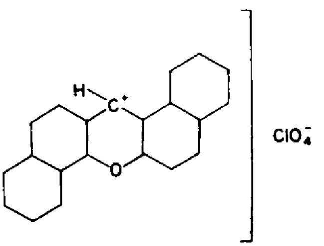


IX

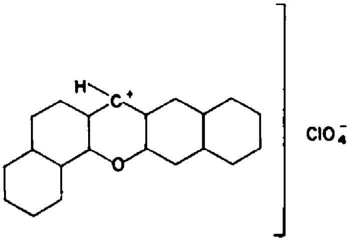


X

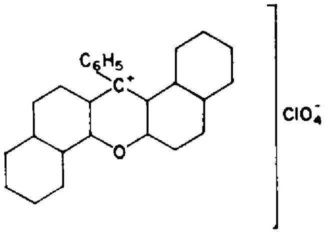
The four dibenzoxanthylium salts (XI–XIV) are readily obtained using the procedure described by Kamel for the preparation of the isomeric 3,4,5,6-dibenzoxanthylium perchlorates (cf. Part I).



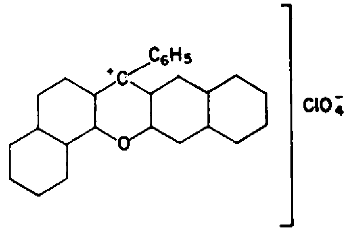
XI; orange, λ_{max} 479 mμ (in acetic acid)



XII; greyish green, λ_{max} 410 and 565 mμ (in acetic acid)



XIII; orange, λ_{max} 483 mμ (in acetic acid)



XIV; greyish green, λ_{max} 430 and 595 mμ (in acetic acid)

A solution of 1,2,5,6-dibenzoxanthylium perchlorate (XI) in acetic acid shows a sharp absorption band in the violet and blue regions of the spectrum with λ_{max} 479 mμ. The same phenomenon is observed in case of 9-phenyl-1,2,5,6-dibenzoxanthylium perchlorate (XIII) but the maximum lies at 483 mμ. The replacement of the hydrogen atom in the position 9 of XI by a phenyl group causes, therefore, a bathochromic effect of 4 mμ. The colour of both perchlorates (XI and XIII) in acetic acid is orange.

A solution of 9-phenylxanthylium perchlorate in acetic acid is yellow (λ_{max} 448 mμ).* This indicates that the annelation of the two benzene rings in positions 1,2- and 5,6- causes a bathochromic shift of 35 mμ towards longer wavelength. It is interesting to mention in this connection that annelation of the same in positions 3,4- and 5,6- causes only a bathochromic shift of 30 mμ (cf. Part I).

On the other hand, a dilute solution of 2,3,5,6-dibenzoxanthylium perchlorate (XII) in acetic acid is greyish green but the concentrated solution is violet red (λ_{max} 410 and 565 mμ). Similarly, a dilute solution of 9-phenyl-2,3,5,6-dibenzoxanthylium perchlorate (XIV) is greyish green and the concentrated solution is violet red (λ_{max} 430 and 595 mμ). The annelation of the two benzene rings in positions 2,3- and 5,6- causes therefore a bathochromic shift of 47 mμ.

EXPERIMENTAL

1-*Hydroxy-2-(2′-naphthyl)naphthoate* (I)†. A mixture of 1-hydroxy-2-naphthoic acid (10 g) and 2-naphthol (7·7 g) was dissolved in xylene (200 ml) by heating at 110–120° for 30 min. Phosphorus oxychloride (10 ml) was then added portionwise during a period of 10 min and heating was continued for 4 hr at the same temp. After cooling, the reaction mixture was stirred into ice-cold water. The xylene layer was washed with water, neutralized (Na_2CO_3 aq.), washed with water again and dried (Na_2SO_4). The oily product obtained after distilling off the xylene was crystallized from benzene as colourless crystals, m.p. 138°, yield 65%. (Found: C, 80·3; H, 4·6. $C_{21}H_{14}O_3$ requires: C, 80·2; H, 4·5%).

The ester (I) is sparingly soluble in pet ether but dissolves in benzene, alcohol and chloroform. It gives a violet colour with alcoholic $FeCl_3$ and a dark yellow colour with conc H_2SO_4.

1,2,5,6-*Dibenzoxanthone* (II). The ester (I, 10 g) was heated for 30 min in a wide-mouthed pyrex tube at 310–315° in a metal-bath. After cooling, the contents of the tube were treated with hot alcohol and the yellow insoluble product crystallized from benzene as yellow needles, m.p. 192°, yield 67%. (Found: C, 85·0; H, 4·4. $C_{21}H_{12}O_2$ requires: C, 85·1; H, 4·1%).

Dibenzoxanthone (II) is sparingly soluble in ether, pet. ether and alcohol. It dissolves in benzene and acetic acid. It is insoluble in NaOH aq. It gives no colour with alcoholic $FeCl_3$, but with conc H_2SO_4 an orange colour is produced (no fluorescence).

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* H. Henkel and R. Wizinger, special communication.

† This ester was previously mentioned in G.P. 43713 (Nencki), but procedure for its preparation or detailed analysis was not given.

1,2,5,6-*Dibenzoxanthene* (V). To 0·75 g pulverized $LiAlH_4$ (Merck), 50 ml dry ether was added. After 15 min, 40 ml dry benzene solution containing 1 g II was added. The reaction mixture was refluxed for 3 hr, then set aside for sometime at room temp. After treatment with cold NH_4Cl aq., the ethereal layer was dried and evaporated. The solid residue was crystallized from benzene to yield 0·9 g 1,2,5,6-dibenzoxanthene (V), m.p. 113°. (Found: C, 89·1; H, 5·2. $C_{21}H_{14}O$ requires: C, 89·3; H, 5·0%). Compound V is insoluble in pet. ether but dissolves in benzene, acetone, alcohol and chloroform. It gives an orange colour with conc. H_2SO_4.

1,2,5,6-*Dibenzoxanthenol* (VII). An amalgam prepared from 0·9 g metallic Na and 75 g Hg was warmed to about 50° in a 400 ml pyrex round-bottomed flask. A cold suspension of 1 g 1,2,5,6-dibenzoxanthone (II) in 150 ml ethyl acetate was added. The flask was at once stoppered, held in a cloth and vigorously shaken for 4 hr, the stopper being raised from time to time to release any pressure. After leaving at room temp overnight, the ethyl acetate solution was separated and evaporated to dryness. The residue was crystallized from benzene to give 1,2,5,6-dibenzoxanthenol (VII), m.p. 234° (sinters at 214°), yield 0·65 g. (Found: C, 84·4; H, 4·8. $C_{21}H_{14}O_2$ requires: C, 84·5; H, 4·7%). Compound VII is sparingly soluble in pet. ether but dissolves in alcohol, benzene and acetone. It dissolves in conc H_2SO_4 with an orange colour (dibenzoxanthylium salt formation).

9-*Phenyl*-1,2,5,6-*dibenzoxanthenol* (IX). To a Grignard solution prepared from 4·5 g bromobenzene and 0·7 g Mg in 50 ml dry ether, a solution of 2 g 1,2,5,6-dibenzoxanthone (II) in 200 ml dry benzene was added gradually during ½ hr. The reaction mixture was heated (steam-bath) for 5 hr and then left at room temp overnight. After treatment with cold NH_4Cl aq., the ether–benzene layer was dried and evaporated. The viscous residue was washed several times with light petroleum (40/60°), then crystallized from benzene to yield 1 g IX, m.p. 236°, green melt. (Found: C, 86·8; H, 5·1. $C_{27}H_{18}O_2$ requires: C, 86·6; H, 4·9%). Compound IX is sparingly soluble in alcohol, acetone and pet. ether but dissolves in benzene. It gives dark orange colour with conc H_2SO_4.

1,2,5,6-*Dibenzoxanthylium perchlorate* XI. To a suspension of VII (0·5 g) in dry benzene, 70% perchloric acid (0·3 ml) was added, and the mixture heated gently for 5 min, whereby, orange yellow crystals were formed. Crystallization from a mixture of acetic acid and acetic anhydride gave XI in quantitative yield, m.p. 233° (dec). (Found: C, 66·5; H, 3·1; Cl, 9·1. $C_{21}H_{13}O_5Cl$ requires: C, 66·2; H, 3·4; Cl, 9·3%). The perchlorate (XI) is sparingly soluble in benzene and pet. ether but dissolves in acetone and acetic acid giving orange solutions (λ_{max} 479 mμ).

9-*Phenyl*-1,2,5,6-*dibenzoxanthylium perchlorate* (XIII). To a suspension of IX (0·5 g) in a mixture of acetic acid and acetic anhydride (8 ml, 1:1), 70% perchloric acid (0·3 g) was added cautiously and the mixture heated gently for 5 min on a steam-bath. On cooling, orange crystals were formed in quantitative yield, m.p. 336° (dec). (Found: C, 71·2; H, 4·0; Cl, 8·1. $C_{27}H_{17}ClO_5$ requires: C, 71·0; H, 3·7; Cl, 7·8%). The perchlorate (XIII) is sparingly soluble in alcohol, benzene, pet. ether and acetone but dissolves in acetic acid giving orange solution. It dissolves in conc H_2SO_4 with an orange red colour (λ_{max} 483 mμ).

3-*Hydroxy*-2-(1′-*naphthyl*)*naphthoate* (III)[2]. This hydroxy ester was prepared from 3-hydroxy-2-naphthoic acid (10 g) and 1-naphthol (7·7 g) in xylene and in presence of phosphorus oxychloride as described above for I.

Crystallization from benzene yielded 7 g of the ester (III), m.p. 128°. It is soluble in alcohol, benzene, chloroform and acetic acid but sparingly soluble in light petroleum. It gives a greenish colour with alcoholic $FeCl_3$ and a yellow colour with conc H_2SO_4.

2,3,5,6-*Dibenzoxanthone* IV. This was prepared in an analogous manner to II by heating the ester (III) at 325° for 45 min. It was repeatedly crystallized from benzene to give pale green needles, m.p. 222°, yield 65%. (Found: C, 85·3; H, 4·2. $C_{21}H_{12}O_2$ requires: C, 85·1; H, 4·1%). The dibenzoxanthone (IV) is sparingly soluble in ether and light petroleum but dissolves in benzene, alcohol and acetic acid. It is insoluble in NaOH aq. It gives no colour with alcoholic $FeCl_3$ but with conc H_2SO_4 a green solution is obtained (no fluorescence).

2,3,5,6-*Dibenzoxanthene* (VI). This was obtained by reducing 2,3,5,6-dibenzoxanthone (IV) with $LiAlH_4$ as described for V. It was crystallized from benzene to give colourless crystals, m.p. 174°, yield quantitative. (Found: C, 88·9; H, 5·1. $C_{21}H_{14}O$ requires: C, 89·3; H, 5·0%). Compound VI is sparingly soluble in light petroleum but dissolves in alcohol, benzene and chloroform. It dissolves in conc H_2SO_4 giving greenish brown solution.

2,3,5,6-*Dibenzoxanthenol* (VIII). For the preparation of this compound, an identical procedure

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[2] E. Jusa and A. V. Janovish, *Mh. Chem.* 71, 186 (1938). *Chem. Abstr.* p. 3617 (1938).

to that used for the preparation of VII was adopted. It was crystallized from benzene to give colourless crystals, m.p. 195°, yield quantitative. (Found: C, 84·6; H, 4·6. $C_{21}H_{14}O_2$ requires: C, 84·5; H, 4·7%). Compound VIII is sparingly soluble in light petroleum but dissolves in acetone, alcohol, benzene and chloroform. It gives a green colour with conc H_2SO_4.

2,3,5,6-*Dibenzoxanthylium perchlorate* XII. This was prepared from 2,3,5,6-dibenzoxanthenol (VIII) in an analogous manner to XI. It was crystallized from nitromethane to give green crystals, m.p. 203°, yield quantitative. (Found: C, 66·4; H, 3·3; Cl, 9·4. $C_{21}H_{13}ClO_5$ requires: C, 66·2; H, 3·4; Cl, 9·3%). Compound XII is sparingly soluble in benzene and pet. ether but dissolves in acetic acid and nitromethane. A dilute solution of XII in acetic acid is greyish green but the concentrated solution is violet red. With conc H_2SO_4 a green colour is obtained, (λ_{max} 410 and 565 mμ).

9-*Phenyl*-2,3,5,6-*dibenzoxanthylium perchlorate* (XIV). 9-Phenyl-2,3,5,6-dibenzoxanthenol (X; 1 g) was dissolved in 50 ml dry benzene and perchloric acid (0·6 ml, 70%) was added. The mixture was heated gently on a water-bath for 5 min, whereby green crystals separated. Crystallization from nitromethane gave glittering crystals, m.p. 279° (dec), yield quantitative. (Found: C, 70·8; H, 4·0; Cl, 7·8. $C_{27}H_{17}ClO_5$ requires: C, 71·0; H, 3·7; Cl, 7·8%). The perchlorate (XIV) is sparingly soluble in benzene and pet. ether but dissolves in nitromethane and acetic acid. A dilute solution of XIV in acetic acid is greyish green but the concentrated solution is violet red. With conc H_2SO_4 a green solution is obtained (λ_{max} 430 and 595 mμ).