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SOME NOVEL RESULTS CONCERNING THE FORMATION OF DIBENZOXANTHONES AND DIBENZODISALICYLIDES FROM *o*-HYDROXYNAPHTHOIC ACIDS AND THEIR DERIVATIVES

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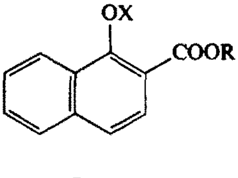
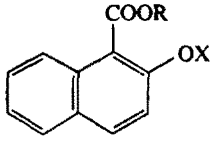
Abstract—Pyrolysis of *o*-hydroxynaphthoic acids (Ia–IIIa), *o*-hydroxyarylnaphthoates (Ib–e–IIIb–e), and *o*-acetoxynaphthoic acids (If–IIIf) has been investigated under different conditions. Whereas, heating of 1-hydroxy-2-naphthoic acid (Ia) and 2-hydroxy-1-naphthoic acid (IIa) gives within certain temperature ranges (among other products), 1-hydroxy-2-(1′-naphthyl)naphthoate (Id) and 2-hydroxy-1-(2′-naphthyl)naphthoate (IIe) respectively; 3-hydroxy-2-naphthoic acid (IIIa) does not yield 3-hydroxy-2-(2′-naphthyl)naphthoate (IIIe). Contrary to prevailing views, *o*-hydroxy-(*p*-cresyl) naphthoates (Ic–IIIc) yield dibenzoxanthones and not methylbenzoxanthones upon heating. 1-Acetoxy-2-naphthoic acid (If) and 3-acetoxy-2-naphthoic acid (IIIf) yield when heated, within certain temperature ranges, dibenzodisalicylide derivatives (IX and X). No dibenzodisalicylide formation was observed in the case of 2-acetoxy-1-naphthoic acid (IIf), 2-hydroxy-1-(2′-naphthyl)-naphthoate (IIe) was formed instead.

The discussion includes brief comments on the mechanism of formation of dibenzoxanthones.

Only a few results are published on the formation of dibenzoxanthones from *o*-hydroxynaphthoic acid and their derivatives. Kostanecki[1] reported that, distillation of acids Ia–IIIa with acetic anhydride gave 3,4,5,6-dibenzoxanthone (IV), 1,2,7,8-dibenzoxanthone (V) and 1,2,6,7-dibenzoxanthone (VI)* respectively. Later, Strohbach[2] found that, heating 3-hydroxy-2-phenylnaphthoate (IIIb) and 3-hydroxy-2-(*p*-cresyl)-naphthoate (IIIc) yielded VI and 7-methyl-2,3-benzoxanthone.†



I



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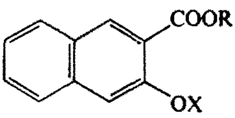

III

In I–IIIa = X = R = H
b = X = H; R = $-C_6H_5$
c = X = H; R = $-C_6H_4\cdot CH_3(p)$
d = X = H; R = $-1\text{-}C_{10}H_7$
e = X H; R = $-2\text{-}C_{10}H_7$
f = X = $-COCH_3$; R = H

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* St. v. Kostanecki originally proposed an incorrect formula for this compound, namely; 2,3,6,7-dibenzoxanthone. Structure VI was established by W. Dilthey and H. Stephan, *J. Prakt. Chem.* **152**, 114 (1939).

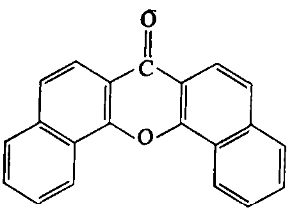
† The formation of methylbenzoxanthone by this method is proved in the present work to be doubtful.

[1] St. v. Kostanecki, *Ber. Dtsch. Chem. Ges.* **25**, 1641 (1892).

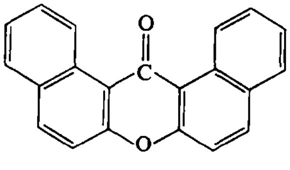
[2] E. Strohbach, *Ber. Dtsch. Chem. Ges.* **34**, 4136 (1901).

Distillation of IIIa in presence of vanadium pentoxide or tungsten trioxide was reported to give VI though an incorrect m.p. was given.[3]

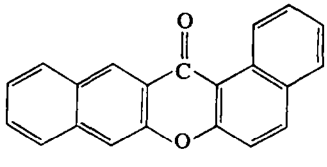
In a previous publication,[4] it was shown that, 3,4,5,6-dibenzoxanthone (IV) can be readily obtained by heating 1-hydroxy-2-naphthoic acid (Ia).



IV

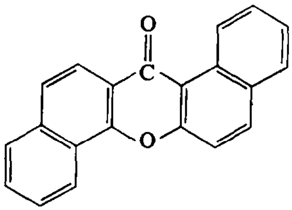


V

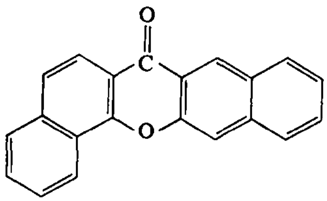


VI

Recently,[5] the hitherto inaccessible mixed dibenzoxanthones: 1,2,5,6-dibenzoxanthone (VII) and 2,3,5,6-dibenzoxanthone (VIII) were prepared by heating 1-hydroxy-2-(2′-napthyl)napthoate(Ie)and 3-hydroxy-2-(1′-naphthyl)naphthoate(IIId) respectively. This simple synthesis opens a direct route for the preparation of a large number of unknown mixed derivatives, e.g., dibenzoxanthydrols, dibenzoxanthenes[6] and dibenzoxanthylium salts.



VII



VIII

In the present study the conditions and formation of dibenzoxanthones from *o*-hydroxynaphthoic acids (Ia–IIIa), their aryl esters (Ib–e–IIIb–e) and acetate derivatives (If–IIIf) by pyrolysis have been investigated.

The behaviour of acids Ia–IIIa and their derivatives on pyrolysis is summarized in Tables 1-3.

Results in Table 1 indicate that, although heating of acids Ia and IIa at 270–300° and IIIa at 325–340° furnish mainly the corresponding naphthols yet reasonable yields of dibenzoxanthones IV–VI (Experimental) are formed and the new procedure is simpler than those previously described for the preparation of dibenenzoxanthones (IV–VI).[7–11] As is seen in Table 1, formation of IV and V starts at ca. 230°, VI at ca.

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[3] G. R. Clemo and R. Spence, *J. Chem. Soc.* 2811 (1928).

[4] M. Kamel, *Helv. Chim. Acta* **42**, 580 (1959).

[5] M. Kamel and H. Shoeb, *Tetrahedron* **20**, 491 (1964).

[6] F. M. Dean and H. D. Locksly, *J. Chem. Soc.* 393 (1963).

[7] G. Bender, *Ber. Dtsch. Chem. Ges.* **19**, 2265 (1886).

[8] A. Claus and W. Ruppel, *J. Prakt. Chem.* [2]**41**, 49 (1890).

[9] R. Fosse, *Bull. Soc. Chim. Fr.* [3]**31**, 250 (1904).

[10] K. Dziewonski and St. Pizon, *Bull. Acad. Polonaise* 406 (1931).

[11] A. Schönberge, R. Moubasher and A. Mostafa, *J. Chem. Soc.* 348 (1941).

TABLE 1. PRODUCTS FORMED BY THE PYROLYSIS OF *o*-HYDROXYNAPHTHOIC ACIDS AT DIFFERENT TEMPERATURE RANGES

1-Hydroxy-2-naphthoic acid				2-Hydroxy-1-naphthoic acid				3-Hydroxy-2-naphthoic acid			
Temp. range	Products	Yields %	Sep. method	Temp. range	Products	Yields %	Sep. method	Temp. range	Products	Yields %	Sep. method
186–190°	Unchanged acid	10		158–188°	Unchanged acid	18·8–1	B.1	223–225°	Unchanged acid		—
	1-Naphthol	62	A.1		2-Naphthol	52·2–42·2		230–320°	Unchanged acid	89·4–6·2	
195–225°	Unchanged acid	5–2·5			Ester IIe†	14–28			2-Naphthol	0–17·6	A.2
	1-Naphthol	49–37	B.1	193–223°	2-Naphthol	43–37·6	G.1		Dibenzoxanthone VI	2·4–44·4	
	Ester Id*	21–34·5			Ester IIe	29·6–33·6		325–340°	2-Naphthol	17·8–14·2	
230–240°	Unchanged acid	2·2–2		228–268°	2-Naphthol	40–49			Dibenzoxanthone VI	26·2–33·5	E
	1-Naphthol	39–41	C		Ester IIe	31·8–8	D				
	Ester Id	32–27			Dibenzoxanthone V	4·4–16					
	Dibenzoxanthone IV	2–5·6		273–300°	2-Naphthol	51·6–55					
245–265°	1-Naphthol	42–46·5			Dibenzoxanthone V	19·2–17·4	G.2				
	Ester Id	23–24	C								
	Dibenzoxanthone IV	9–23									
270–300°	1-Naphthol	46·7–51									
	Dibenzoxanthone IV	25–22	E								

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* 1-Hydroxy-2-(1′-naphthyl)naphthoate (Id) crystallizes from MeOH as pale yellow crystals, m.p. 97–98° (cinters at 94°, unclear melt). The m.p. was undepressed on admixture with an authentic sample prepared as described below (cf. page 8 & 9). (Found: C, 80·10; H, 4·63. $C_{21}H_{14}O_3$ requires: C, 80·32; H, 4·48%). Id is readily soluble in ether, benzene, chloroform and alcohol. It gives a greenish yellow colour with alcoholic $FeCl_3$ and a brownish colour with conc. H_2SO_4. It is hydrolysed with alcoholic NaOH (10%) to give 1-naphthol and acid Ia. Boiling with acetic anhydride gives 1-acetoxy-2-(1′-naphthyl)-naphthoate, colourless needles from alcohol, m.p. 175°. (Found: C, 77·88; H, 4·82. $C_{23}H_{16}O_4$ requires: C, 77·51; H, 4·4).

† 2-Hydroxy-1-(2′-naphthyl)naphthoate (IIe) crystallizes from alcohol as colourless needles, m.p. 154° (m.p. undepressed when admixed with an authentic sample prepared as described below (cf. page 8 & 9). (Found: C, 80·21; H, 4·63. $C_{21}H_{14}O_3$ requires: C, 80·32; H, 4·48%). IIe is readily soluble in alcohol, benzene, chloroform and acetone. It gives a greenish yellow colour with alcoholic $FeCl_3$ and a brownish colour with conc. H_2SO_4. It is hydrolysed when boiled with alcoholic NaOH (10%) giving 2-naphthol and acid IIa. Boiling with acetic anhydride gives 2-acetoxy-1-(2′-naphthyl)naphthoate. Colourless needles from alcohol m.p. 186°. (Found: C, 77·42; H, 4·63. $C_{23}H_{16}O_4$ requires: C, 77·51; H, 4·54%).

240° but if salicylic acid is heated at 250°, xanthone, phenol and unchanged acid are obtained.[12]

Pyrolysis of Ia between 230–265°, yields 1-naphthol, 1-hydroxy-2-(1′-naphthyl)-naphthoate (Id) and dibenzoxanthone IV. Acid IIa behaves similarly on pyrolysis between 228–268°, and gives mixtures of 2-naphthol, 2-hydroxy-1-(2′-naphthyl)-naphthoate (IIe) and dibenzoxanthone (V). Both Id and IIe disappear from pyrolysis mixtures obtained above 270°, presumably, due to transformation into IV and V respectively.

Furthermore, it is found that, Ia and IIa yield mixtures of the corresponding naphthol, the corresponding *o*-hydroxynaphthyl esters besides unchanged acids, if the former is heated at temperatures between 195–225° and the latter between 158–188°.

Formation of both Id and IIe, presumably, proceeds by interaction of 1-naphthol and 2-naphthol (formed by decarboxylation) with Ia and IIa. This is analogous to the formation of salol when salicylic acid is heated for a long time at 200–220°.[12] The structure of Id and IIe was inferred from: (a) the correct analytical figures; (b) the formation of acetate derivatives; (c) the formation of Ia and 1-naphthol; IIa and 2-naphthol on hydrolysis; (d) the identity with authentic samples prepared from Ia and 1-naphthol; IIa and 2-naphthol; (e) the greenish yellow colour produced with alcoholic ferric chloride.

When Ia is heated below or just above its m.p. (186°), it decomposes into 1-naphthol and carbon dioxide. The degree of decomposition increases with increase of temperature and duration of heating—nearly complete decomposition taking place after 60 min at 186° and therefore, formation of Id is not favoured at this temperature. On the other hand, IIa gives upon heating at its m.p. (158°) mixtures of unchanged acid, 2-naphthol and IIe.

In contrast, acid IIIa on pyrolysis yields only 2-naphthol and VI even when heated at its m.p. (223°). This may be due to the fact that the m.p. lies within the temperature range where the formation of VI is favoured.

The three acids Ia–IIIa differ also in their stability at higher temperatures; whereas, acids Ia and IIa disappear completely when pyrolysis is carried out above 245 and 193° respectively, acid IIIa starts to disappear completely at 325°.

The behaviour of phenyl, *p*-cresyl, 1-naphthyl and/or 2-naphthyl esters of the above acids on pyrolysis at different temperatures is given in Table 2.

As shown in Table 2, dibenzoxanthones are the only xanthone derivatives formed by heating these derivatives at ca. 300°. This partially contradicts Strohbach[2] who claimed that the pyrolysis of the three *p*-cresyl esters (Ic–IIIc) should lead to the formation of the corresponding methylbenzoxanthones and that 7-methyl-2,3-benzoxanthone was obtained upon boiling IIIc for 10 hr. However, dibenzoxanthone (VI) was obtained from this *p*-cresyl ester under the experimental conditions used by Strohbach.

The pyrolysis of three phenyl esters (Ib–IIIb) and naphthyl esters (Id,e–IIId,e) conforms with Strohbach's rules and leads to the formation of the corresponding dibenzoxanthones as indicated in Table 2.

Pyrolysis of all the phenyl and *p*-cresyl esters used shows that the phenyl and *p*-cresyl radicals do not share in the formation of the dibenzoxanthones (IV, V and VI) and that the *o*-hydroxynaphthoic radical determines the type of dibenzoxanthone

[12] C. Graebe and A. Eichengrün, *Liebegs. Ann.* **269**, 324 (1892).

TABLE 2. PRODUCTS FORMED BY THE PYROLYSIS OF *o*-HYDROXYARYL ESTERS AT DIFFERENT TEMPERATURE RANGES

o-Hydroxyaryl ester	Temp range	Products	Yields %	Separation method
Ib	96–270°	Unchanged ester		—
	295–300°*	Phenol	30	E
		Dibenzoxanthone IV	40	
Ic	92–270°	Unchanged ester		—
	295–300°*	p-Cresol	32	E
		Dibenzoxanthone IV	42	
Id	97–205°	Unchanged ester		—
	210–270°	Unchanged ester	80–87	
		1-Naphthol	0–11	C
		Dibenzoxanthone IV	5·4–64	
	275–300°	1-Naphthol	14–25·6	
		Dibenzoxanthone IV	68–56·1	E
IIb	86–270°	Unchanged ester		—
	295–300°*	Phenol	28	E
		Dibenzoxanthone V	46	
IIc	91–270°	Unchanged ester		—
	295–300°*	p-Cresol	32	E
		Dibenzoxanthone V	42	
IId	124–170°	Unchanged ester	92·5–73·1	D
		1-Naphthol	0–85	
	175–265°	Unchanged ester	71·4–1·1	
		1-Naphthol	5·9–13·9	D
		Dibenzoxanthone VII	2·7–61·8	
	270–300°	1-Naphthol	14·2–31	E
		Dibenzoxanthone VII	61–57	
IIe	154–160°	Unchanged ester	79·5–56·8	D
		2-Naphthol	6·1–8·5	
	165–270°	Unchanged ester	51·3–1·1	
		2-Naphthol	9–27·8	D
		Dibenzoxanthone V	9·8–45·5	
	275–300°	2-Naphthol	28·2–30·9	E
		Dibenzoxanthone V	44·4–33·3	
IIIc	90–270°	Unchanged ester		—
	295–300°*	p-Cresol	34	E
		Dibenzoxanthone VI	43	
IIIe	138–210°	Unchanged ester	86–64·2	D
		2-Naphthol	5·8–23·6	
	215–325°	Unchanged ester	62–7·8	
		2-Naphthol	24–12	D
		Dibenzoxanthone VI	14–59	

* In these cases the pyrolysis experiments were carried out for 4 hr instead of 30 min.

formed. On the other hand, all the naphthyl esters used show that the naphthyl radical contributes in the formation of the corresponding dibenzoxanthone. As a result, it is now possible to synthesize the mixed dibenzoxanthone (VII) by the pyrolysis of the two mixed naphthyl esters (Ie and IId).

Furthermore, pyrolysis of all the esters used, in addition to dibenzoxanthones, yield a certain amount of the parent phenol or naphthol taking part in their structure.

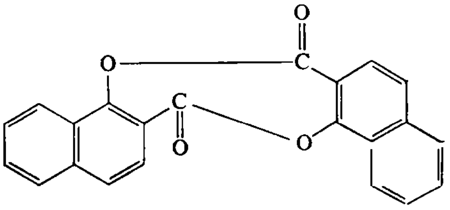
Kostanecki reported that IV, V and VI are obtained when Ia, IIa and IIIa are distilled with acetic anhydride, but he failed to specify whether he meant distillation of the acetic anhydride only or distillation of the whole mixture. Moreover, the author did not indicate any possible mechanism for this reaction.

It is found that: (a) distillation of acetic anhydride alone from the mixture does not give any dibenzoxanthone but leaves the acetoxy acid as the sole product; (b) distillation of the acetoxy acid results mainly in charring and formation of poor yields of dibenzoxanthones; (c) the best yields may be obtained if after removal of the acetic anhydride, the residual acetoxy acid is only heated at 270–300° and not distilled.

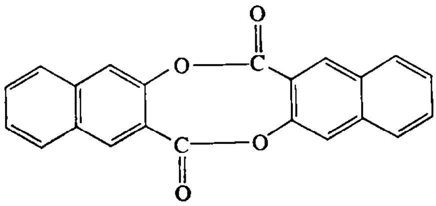
The behaviour of the three acetoxy acids (If, IIf and IIIf) on pyrolysis at different temperatures are summarized in Table 3.

It is clear from Table 3 that If undergoes gradual transformation into 3,4,7,8-dibenzodisalicylide (IX) if it is pyrolysed at 143–210°. Within the range 205–210°, If is transformed into IX quantitatively. Above 215° and up to 250°, mixtures containing IX and dibenzoxanthone IV are obtained. At temperatures between 255–270°, IV is the only product and above 270°, IV partially decomposes into l-naphthol.

Acid IIIf behaved similarly with the exception that 2,3,6,7-dibenzodisalicylide (X) is stable at higher temperatures (ca. 295°).

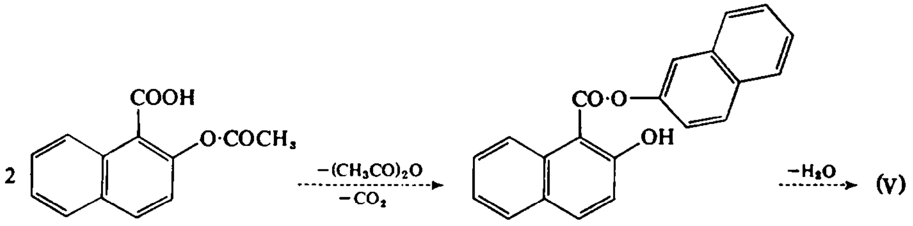


IX



X

The behaviour of acid is IIf different in that 2-hydroxy-1-(2′-naphthyl)naphthoate (IIe) is the only intermediate product formed before the dibenzoxanthone formation.



Proof of the structure of compounds IX and X is based on: (a) the correct analytical figures; (b) the formation of acids Ia and IIIa respectively on hydrolysis with alcoholic NaOH; (c) the absence of any colour formation with alcoholic ferric chloride.

The dibenzodisalicylide IX and X are the first examples in the literature of this group of compounds. Jusa and Janovich[13] prepared an impure product supposed to be X by estrification of IIIa with itself using phosphorous oxychloride. Seifert[14] and later Strohbach[2] assumed the formation of these products as intermediates during formation of xanthone derivatives but were never successful in obtaining them.

[13] E. Jusa and A. V. Janovich, *Mh. Chem.* **71**, 186 (1938). *Chem. Abstr.* 3617 (1938).

[14] R. Seifert, *J. Prakt. Chem.* [2]**31**, 478 (1885).

Table 3. Products formed by the pyrolysis of *o*-acetoxynaphthoic acids at different temperature ranges

1-Acetoxy-2-naphthoic acid			
Temp. range	Products	Yields %	Sep. method
143–200°	Unchanged acid	86–5	G.2
	Dibenzodisalicylide IX*	3–65	
205–210°	Dibenzodisalicylide IX	79	—
215–250°	Dibenzodisalicylide IX	64–6	F
	Dibenzoxanthone IV	6–52	
255–270°	Dibenzoxanthone IV	59	—
275–300°	1-Naphthol	1–2·3	E
	Dibenzoxanthone IV	57–46·3	

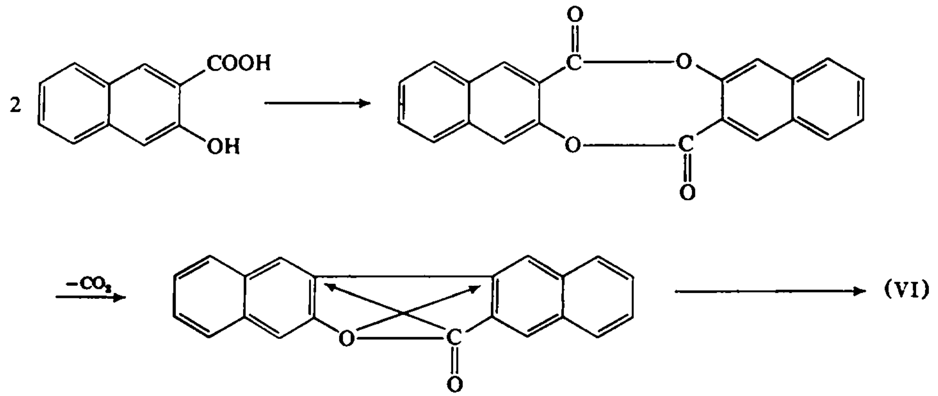
2-Acetoxy-1-naphthoic acid			
Temp. range	Products	Yields %	Sep. method
132–215°	Unchanged acid	35·2–19·2	B.2
	2-Naphthol	24·5–18·6	
	Ester IIe	13·4–27·8	
220–240°	Unchanged acid	18·2–5·6	B.2
	2-Naphthol	18·8–27·6	
	Ester IIe	28–18·4	
	Dibenzoxanthone V	3–7·8	
245–270°	2-Naphthol	29·2–32·4	B.2
	Ester IIe	18·8–5·6	
	Dibenzoxanthone V	11·6–26·4	
275–300°	2-Naphthol	32·4–32·8	E
	Dibenzoxanthone V	36–31·6	

3-Acetoxy-2-naphthoic acid			
Temp. range	Products	Yields %	Sep. method
180–205°	Unchanged acid	67·6–1·4	A.2
	Dibenzodisalicylide X†	19–66·2	
210–220°	Dibenzodisalicylide X	70·69	—
225–300°	Dibenzodisalicylide X	56·6–10·6	F
	Dibenzoxanthone VI	0·8–47·6	

* 3,4,7,8-Dibenzodisalicylide (IX) crystallizes from benzene–pet. ether as colourless crystals, m.p. (cintering between 190–195° without giving a clear melt). (Found: C, 78·25; H, 3·61. $C_{22}H_{12}O_4$ requires: C, 77·64; H, 3·55%.) IX is sparingly soluble in ether, light petroleum and alcohol but dissolves in benzene and chloroform. It does not give any colour with alcoholic $FeCl_3$ but gives with conc. H_2SO_4 a brownish orange colour. Hydrolysis with alcoholic KOH (10%) gives 1-hydroxy-2-naphthoic acid (Ia) alone.

† 2,3,6,7-Dibenzodisalicylide X crystallizes from benzene–pet. ether as colourless crystals, m.p. (cintering at 202–205° but not melting completely). (Found: C, 77·17; H, 3·72. $C_{22}H_{12}O_4$ requires: C, 77·64; H, 3·55%.) X is sparingly soluble in ether, alcohol and pet. ether, but dissolves in benzene, chloroform and acetone. It does not give any colour with alcoholic $FeCl_3$. It gives a brownish orange colour with conc. H_2SO_4. It is hydrolysed with alcoholic KOH (10%) giving 3-hydroxy-2-naphthoic acid (IIIa) alone.

The mechanism of formation of xanthone and its derivatives has been the subject of many theories and contradictory views.[5,12,14,15] The isolation of dibenzodisalicylide derivatives (IX and X) is in agreement with Strohbach's views who considered that VI is formed from IIIa as follows:



In conclusion, pyrolysis of *o*-hydroxynaphthoic acids, their phenyl, *p*-cresyl and naphthyl esters as well as their acetate derivatives always give dibenzoxanthones at temperatures of about 300°. The best yields of dibenzoxanthones are obtained by pyrolysis of naphthyl esters. The mechanism of formation of these compounds is not identical in all cases, and further work is necessary before any final conclusions may be drawn.

EXPERIMENTAL

General method for preparation of o-hydroxyarylnaphthoates

A mixture of *o*-hydroxynaphthoic acid (0·05 mole) and phenol or naphthol (0·05 mole) was dissolved in dry xylene or benzene by heating at 110–120° for 30 min. A condensing agent ($POCl_3$, PCl_5 or P_2O_5; 15–20 g) was then added portionwise during a period of 10 min and heating was then continued during 4 hr at the same temp. After cooling, the reaction mixture was stirred into ice-cold water. The xylene or benzene layer was then washed with water, neutralized with Na_2CO_3aq, washed with water again and dried (Na_2SO_4). The oily product obtained after distilling off the xylene or benzene was treated with MeOH and crystallized from alcohol as colourless crystals. All *o*-hydroxyarylnaphthoates prepared in this communication are soluble in ether, benzene, chloroform and acetone

General procedure and general remarks for pyrolysis

A pyrex glass tube (cap. 250 ml) containing 10 g of the substance to be pyrolysed was placed in a molten metal-bath at 100°. The temp of the latter was raised slowly within 10–20 min to the desired temp, which was kept constant for another 30 min (unless otherwise stated). The tube was cooled, and the components of the pyrolysis mixture separated and identified.

Two pyrolysis experiments were carried out, each 5° between the m.p. of the substance and 300°, and the mean of the yields was taken. For simplification, similar pyrolysis results are shown in Tables 1, 2 and 3 under one temp range, yields (%) of the lowest and highest temp within each range only are given.

Methods of separation

Method A. A.1. After pyrolysis had been completed, the contents of the tube were dissolved in ether (100 ml). The ethereal solution was then treated with 10% Na_2CO_3aq, washed with water, dried (Na_2SO_4) and evaporated. The residue was crystallized from pet. ether and identified.

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[15] S. Nath Dhar, *J. Chem. Soc.* 117, 1053 (1920).

TABLE 4. *o*-HYDROXYARYLNAPHTHOATES

o-Hydroxyarylnaphthoates	m.p.	Yield %	Colour with alcoholic $FeCl_3$	Colour with conc. H_2SO_4	Analysis %
1-Hydroxy-2-phenyl-naphthoate (Ib)	96°	57	bluish	yellow	Found: C, 77·09; H, 4·68. $C_{17}H_{12}O_3$ requires: C, 77·25; H, 4·57.
1-Hydroxy-2-(p-crysyl)-naphthoate (Ic)	96–97°	50	bluish	yellow	Found: C, 77·78; H, 5·04. $C_{18}H_{14}O_3$ requires: C, 77·68; H, 5·07.
1-Hydroxy-2-(1′-naphthyl)-naphthoate (Id)	97–98° cinters at 94°	46	yellowish green	orange	Found: C, 80·16; H, 4·53. $C_{21}H_{14}O_3$ requires: C, 80·23; H, 4·48.
2-Hydroxy-1-phenyl-naphthoate (IIb)	86°	43	yellowish green	yellow	Found: C, 77·02; H, 4·49. $C_{17}H_{12}O_3$ requires: C, 77·25; H, 4·57.
2-Hydroxy-1-(p-cresyl)-naphthoate (IIc)	90–92°	40	yellowish green	yellow	Found: C, 77·97; H, 5·07. $C_{18}H_{14}O_3$ requires: C, 77·68; H, 5·07.
2-Hydroxy-1-(1′-naphthyl)-naphthoate (IId)	123–124°	66	yellowish green	light red	Found: C, 80·58; H, 4·66. $C_{21}H_{14}O_3$ requires: C, 80·23; H, 4·48.
2-Hydroxy-1-(2′-naphthyl)-naphthoate (IIe)	154°	76	yellowish green	light red	Found: C, 79·65; H, 4·58. $C_{21}H_{14}O_3$ requires: C, 80·23; H, 4·48.

The carbonate solution was acidified (HCl) and the precipitated naphthoic acid was identified.

A.2. Similar to (A.1) except that the pyrolysis mixtures were dissolved in a mixture of benzene and ether (200 ml; 1:1) instead of ether alone.

Method B. B.1. Similar to method A.1 except that the residue obtained on evaporation of ether was fractionally crystallized from MeOH.

B.2. Similar to B.1 except that the pyrolysis mixture was dissolved in benzene (250 ml) instead of ether.

Method C. Pyrolysis mixtures were treated with ether, the ether insoluble fraction (dibenzoxanthone) filtered off. The ethereal solution was worked up as under B.1.

Method D. Trials to fractionate the pyrolysis mixtures into their components using fractional crystallization failed. An indirect method for determination of the yields was used:
Pyrolysis mixtures were boiled with a solution of 10% NaOHaq for 1 hr and the insoluble fraction (dibenzoxanthone) filtered off. The alkaline filtrate was acidified and worked up as under B.1. From the quantities of the hydroxynaphthoic acid and 2-naphthol obtained, the yield of IIe was calculated.

Method E. The pyrolysis mixtures were treated with ether only and the insoluble fraction (dibenzoxanthone) filtered off. The ethereal solution was evaporated and the residue identified.

Method F. Mixtures of dibenzodisalicylide and dibenzoxanthone were obtained. Trials to separate them by fractional crystallization failed. The estimation of the yields of the two products was carried out as follows: the pyrolysis mixture was first weighed out and then boiled with a solution of 10% KOHaq during 30 min. The insoluble fraction was identified as dibenzoxanthone. Yields of the dibenzodisalicylide were calculated by difference.

Method G. G.1. Pyrolysis mixtures were fractionally crystallized from MeOH.

G.2. Pyrolysis mixtures were fractionally crystallized from EtOH.