

J. A. Van Allan, J. F. Stenberg and G. A. Reynolds

Research Laboratories, Eastman Kodak Company, Rochester, New York 14650

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Certain chromones and benzoxanthenes were prepared by heating at 300-325° a mixture of 1- or 2-naphthol with either phenyl *o*-hydroxybenzoate or *o*-hydroxynaphthoate or a β -ketoester. The yields and purity of the products are superior to those obtained by the published procedures.

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Recent work by Perlstein (1,2) has indicated that certain *bis*-chromylenes and *bis*-xanthylenes may form mixed-valence charge-transport entities when complexed with tetracyanoquinomethane (TCNQ) or iodine. The synthesis of *bis*-chromylenes and xanthylenes requires chromones and xanthenes as precursors, and the present report describes their synthesis. Kamel and Schoeb (3) have reviewed the literature relative to the synthesis of the dibenzoxanthenes and in a comprehensive paper have examined in detail the pyrolysis of *o*-hydroxynaphthoic acid and *o*-hydroxynaphthoates. They describe their general procedure as follows: "A 250 ml. Pyrex glass tube containing 10 g. of the substance to be pyrolyzed was placed in a metal bath at 100°. The temperature of the latter was slowly raised within 10-20 minutes to the desired temperature (which is critical for each compound and is in the range of 250-300°) and kept constant for another 30 minutes (unless otherwise stated). The tube was cooled and the components of the pyrolysis mixture separated and identified." This procedure is not suitable for the production of large quantities of these materials. We now report a method which makes these xanthenes easily available in fair to good yields.

We heated equivalent quantities of phenyl salicylate or *o*-hydroxynaphthoate and a naphthol in Marlotherm S (4) for 3-20 hours at 300-325°. The phenol was removed as it was formed. After cooling, a suitable diluent (ether or toluene) was added, and the product was isolated by filtration. The yields were 33-70%. The crude product in most cases could be used without further purification. Table I summarizes the xanthenes prepared by this procedure.

The dibenzoxanthone (8) may also be prepared in 93% crude yield by heating phenyl 1-hydroxy-2-naphthoate (2) in diphenyl ether at 260° for 20 hours or in Marlotherm S at 310° for the same time. Phenyl 2-hydroxy-3-naphthoate (3) remains unchanged under these conditions.

We have extended the reaction of naphthols with hydroxy naphthoates to the preparation of some benzo chromones. Ethyl benzoylacetate (12) and ethyl acetoacetate 13 were used in place of the phenyl hydroxy naphthoates. Table II summarizes the chromones prepared from 1-naphthol and 2-naphthol and the esters 12 and 13.

EXPERIMENTAL

Phenyl salicylate (1), phenyl 1-hydroxy-2-naphthoate (2), 1-naphthol (4) and 2-naphthol (5) were obtained from Eastman Organic Chemicals. Phenyl 2-hydroxy-3-naphthoate (3) was prepared by published procedures (3,5).

14*H*-Dibenzo[*a,i*]xanthen-14-one (11).

A mixture of 105.6 g. (0.4 mole) of 3 and 64 g. (0.44 mole) of 5 in 250 ml. of Marlotherm S (4) was heated at 300-325° for 20 hours. During the first 4 hours, 35 ml. of phenol was collected. The hot reaction mixture was poured into a beaker, cooled to about 100° and diluted with 200 ml. of a 1:1 mixture of toluene and ligroin. After cooling to room temperature, the product was collected and washed with ligroin, giving 81 g. (70%) of 11, m.p. 241-243°. Recrystallization from pyridine raised the m.p. to 249-250° (reported 244-246° (6)).

The following xanthenes and chromones were prepared by the method described for the preparation of 11 except the heating periods were those reported in Tables I and II.

7*H*-Benzo[*c*]xanthen-7-one (6).

This compound was recrystallized from a mixture of pyridine and methanol. The reported m.p. was 155° (7).

12*H*-Benzo[*a*]xanthen-12-one (7).

The reported m.p. was 145° (8).

7*H*-Dibenzo[*c,h*]xanthen-7-one (8).

The reported m.p. was 243° (4).

14*H*-Dibenzo[*a,h*]xanthen-14-one (9).

The compound was recrystallized from benzene. However, the crude product was a 1:1 mixture of 9 and 8, and one crystallization was not sufficient to separate the mixture. A pure sample of 9 (m.p. 242-243°) was obtained by chromatographing on alumina, eluting with methylene chloride. The reported m.p. (3) was 192°, but we think this was of a mixture of 8 and 9.

The nmr for 9 (deuteriochloroform) was: δ 8.64 (q, 1H) for H-8; δ 8.33 (d, 1H) for H-6, δ 8.12 (d, 1H) for H-13; and δ 7.5-7.9 (m, 9H).

The nmr for 8 (deuteriochloroform) was: δ 8.48 (q, 2H) for H-1 and H-13; δ 8.15 (d, 2H) for H-6 and H-8; and 7.43-7.75 (m, 8H).

Anal. Calcd. for C₂₁H₁₂O₂: C, 85.1; H, 4.1. Found: C, 84.9; H, 4.4.

7*H*-Dibenzo[*b,h*]xanthen-7-one (10).

The m.p. of the crude product was 219-220°, which was raised to 222-224° by recrystallization from a mixture of pyridine and methanol. The reported m.p. was 222° (4).

3-Methyl-1*H*-naphtho[2,1-*b*]pyran-1-one (14).

The reported m.p. was 168° (9).

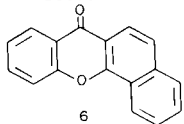
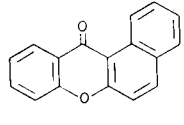
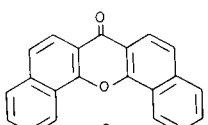
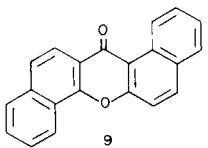
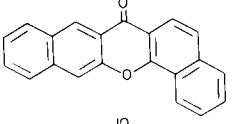
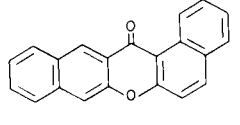
3-Phenyl-1*H*-naphtho[2,1-*b*]pyran-1-one (15).

The reported m.p. was 164-165° (10).

2-Methyl-4*H*-naphtho[1,2-*b*]pyran-4-one (16).

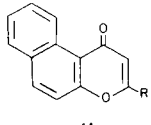
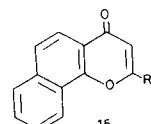
The reported m.p. was 181° (9).

Table I
Xanthenes

Components (a)	Product	M.p. °C	Hours Heating	% Yield
1 + 4	 6	160	5	51
1 + 5	 7	143-144	20	51
2 + 4	 8	251-253	3	33
2 + 5	 9	242-243	3	34
3 + 4	 10	222-224	20	60
3 + 5	 11	249-250	20	70

(a) (1) Phenyl salicylate, (2) phenyl 1-hydroxy-2-naphthoate, (3) phenyl 2-hydroxy-3-naphthoate, (4) 1-naphthol, (5) 2-naphthol.

Table II
Chromones

Components	Product	M.p. °C	Hours Heating	% Yield
12 + 4	14 R = CH ₃	166	4	10
12 + 5	15 R = C ₆ H ₅	165	3	45
	 14			
	 15			
13 + 4	16 R = CH ₃	181	2	25
13 + 5	17 R = C ₆ H ₅	156	5	65

2-Phenyl-4H-naphtho[1,2-b]pyran-4-one (17).

Two melting points have been reported for this compound: 155-156° (11) and 167° (10).

7H-Dibenzo[*c,h*]xanthen-7-one (8).

A mixture of **2** (100 g.) and 300 ml. of Marlotherm S was heated with stirring at 300-310°. During the first hour, 26 ml. of distillate was collected. After 3 hours, the mixture was poured into a beaker, cooled, diluted with toluene and the solid was collected. The crude product (37 g., m.p. 225-230°) was recrystallized from *o*-dichlorobenzene, giving 34 g. of **8**, m.p. 251-252°.

Acknowledgement.

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