345. *Chromones of the Naphthalene Series. Part II. Synthesis of Linear Naphthaflavone(6 : 7-Benzoflavone).*

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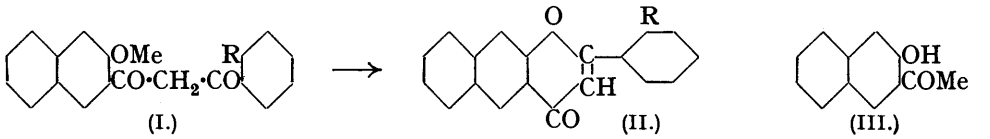
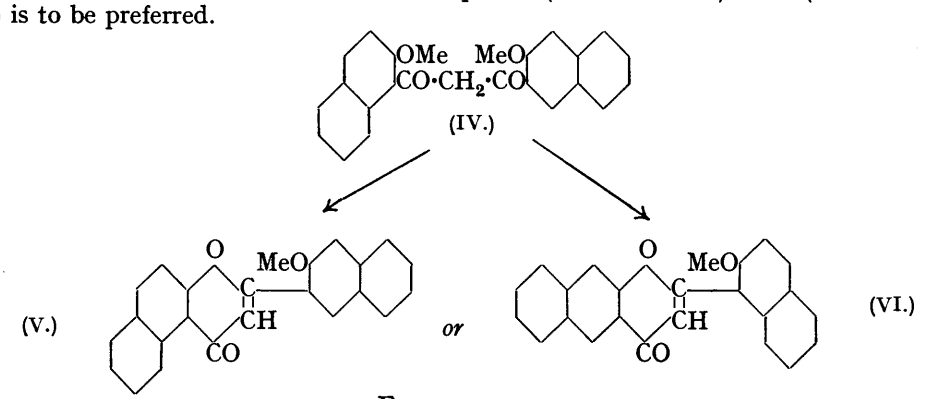
The synthesis of 6 : 7-*benzoflavone* and other chromones of the naphthalene series by cyclisation of the corresponding *o*-alkoxydiaroylmethanes by Kostanecki's method is described. 6 : 7-Benzoflavones give 2-hydroxy-3-acetonaphthone on treatment with alcoholic sodium ethoxide.

o-ALKOXYDIAROYLMETHANES of the naphthalene series have been synthesised by the Claisen method from the corresponding acetoarones and alkyl aroates; cyclisation to *chromones* by Kostanecki's method is effected with hydrogen bromide in acetic acid, or by the action of hydriodic acid in acetic anhydride, regulated so that dealkylation of alkoxy-groups beyond that required for cyclisation is avoided. 6 : 7-*Benzoflavone* (II; R = H), obtained in this way from *benzoyl*-2-*methoxy*-3-*naphthoylmethane* (I; R = H), and its 2′-*methoxy*-derivative (II; R = OMe), on treatment with alcoholic sodium ethoxide gave 2-hydroxy-3-acetonaphthone (III), a compound not readily accessible (cf. Baker and Carruthers, J., 1937, 482), and 2-hydroxy-3-naphthoic acid (for the course of reactions of this type see Kostanecki and Feuerstein, *Ber.*, 1898, **31**, 1757; Kostanecki and Ludwig,

ibid., p. 2951). The production of (III) from (II; R = OMe) establishes the course of the cyclisation of o-*anisoyl*-2-*methoxy*-3-*naphthoylmethane* (I; R = OMe).



The preparation of some 2-naphthylbenzochromones is also described; a compound of this type has been synthesised (cf. Röthlisberger, *Helv. Chim. Acta*, 1925, **8**, 112) by the Kostanecki chalkone dibromide method. The *product* obtained by the cyclisation of 2 : 3′-*dimethoxy*-1 : 2′-*dinaphthoylmethane* (IV) is either (V) or (VI); as it was resistant to the action of alcoholic sodium ethoxide and aqueous potassium hydroxide even under drastic conditions, it was not possible definitely to decide between the alternative structures. In view of the formation of the linear compound (II; R = OMe) from (I; R = OMe), (VI) is to be preferred.



Experimental.

o-*Alkoxydiaroylmethanes.*—*Benzoyl*-2-*methoxy*-3-*naphthoylmethane* (1). A solution of acetophenone (8 g.) and methyl 2-methoxy-3-naphthoate (14 g.) (Werner and Seybold, *Ber.*, 1904, **37**, 3661) in dry ether (35 c.c.) was added in small quantities under cooling to a suspension of pulverised sodium (1·5 g.) in ether (5 c.c.). The mixture was shaken at intervals for 3 hours and kept overnight, ether removed (water-pump), and the residue treated with dilute acetic acid. The product separated from alcohol in yellow plates, m. p. 98° (Found: C, 78·7; H, 5·3. $C_{20}H_{16}O_3$ requires C, 78·9; H, 5·3%).

o-*Anisoyl*-2-*methoxy*-3-*naphthoylmethane* (2), m. p. (light petroleum) 120—122° (Found: C, 75·2; H, 5·6. $C_{21}H_{18}O_4$ requires C, 75·4; H, 5·4%), 3-*methoxydi*-2-*naphthoylmethane* (3), m. p. (acetone) 160° (Found: C, 81·3; H, 5·1. $C_{24}H_{18}O_3$ requires C, 81·3; H, 5·1%), *di*-(1-*methoxy*-2-*naphthoyl*)*methane* (4), m. p. (alcohol) 122° (Found: C, 77·8; H, 5·3. $C_{25}H_{20}O_4$ requires C, 78·1; H, 5·2%), and 2 : 3′-*dimethoxy*-1 : 2′-*dinaphthoylmethane* (5), m. p. (benzene–absolute alcohol) 163° (Found: C, 78·0; H, 5·3. $C_{25}H_{20}O_4$ requires C, 78·1; H, 5·2%) were similarly prepared from *o*-methoxyacetophenone and methyl 2-methoxy-3-naphthoate, 2-acetonaphthone and methyl 2-methoxy-3-naphthoate, 1-methoxy-2-acetonaphthone (Heilbron, Hey, and Lowe, J., 1934, 1314) and methyl 1-methoxy-2-naphthoate (Froelicher and Cohen, J., 1922, **121**, 1656), and 2-methoxy-1-acetonaphthone (Noller and Adams, *J. Amer. Chem. Soc.*, 1924, **46**, 1892) and methyl 2-methoxy-3-naphthoate respectively. These diketones are yellow; they are insoluble in aqueous alkali but readily soluble in alcoholic alkali.

Bromo-o-*anisoyl*-2-*methoxy*-3-*naphthoylmethane* (6 g.), m. p. (acetic acid) 152° (Found: Br, 18·9. $C_{21}H_{17}O_4Br$ requires Br, 19·3%), remained after removal of the solvent from a solution of (2) (5 g.) in chloroform (50 c.c.) through which had been passed a current of air which had previously been led through a solution of bromine (2·5 g.) in chloroform (20 c.c.). With a view to the synthesis of flavonols unsuccessful attempts were made to replace bromine by acetoxyl with a solution of anhydrous sodium acetate in acetic acid (cf. Neufville and Pechmann, *Ber.*, 1890, **23**, 3377).

Preparation of 2-*Arylbenzochromones.*—6 : 7-*Benzoflavone* (linear naphthaflavone) (6) (0·25 g.), m. p. (benzene) 171—172° (Found: C, 83·9; H, 4·5. $C_{19}H_{12}O_2$ requires C, 83·8; H, 4·4%),

separated when a solution of (1) (0·5 g.) in acetic anhydride (5 c.c.), which had been treated with hydriodic acid (*d* 1·7; 5 c.c.), and heated under reflux for 1 hour, was poured into aqueous sodium hydrogen sulphite solution. (6) was also obtained when a solution of (1) and of hydrogen bromide in acetic acid, which had been heated at 100° for 6 hours, was poured into water.

Treatment of (6) *with alcoholic sodium ethoxide; preparation of* 2-*hydroxy*-3-*acetonaphthone.* An aqueous solution of the precipitate obtained by heating a solution of (6) (1 g.) and of sodium ethoxide (2 g. of sodium) in alcohol (50 c.c.) under reflux for 4 hours gave on saturation with carbon dioxide a precipitate of 2-hydroxy-3-acetonaphthone (0·3 g.), m. p. (light petroleum) 112°; acetyl derivative, m. p. 100° (lit. 112° and 101°). Addition of hydrochloric acid to the filtrate from which the hydroxyacetonaphthone had been removed precipitated 2-hydroxy-3-naphthoic acid, the m. p. of which was not depressed by addition of an authentic specimen.

2′-*Methoxy*-6 : 7-*benzoflavone* (7) (0·5 g.), m. p. (alcohol) 165° (Found: C, 79·6; H, 4·8. $C_{20}H_{14}O_3$ requires C, 79·5; H, 4·6%), was precipitated when a solution of (2) (1 g.) and of hydrogen bromide in acetic acid (12 c.c.), which had been kept overnight, was poured into water. 2′-*Hydroxy*-6 : 7-*benzoflavone* (8) (0·2 g.), m. p. (nitrobenzene) 256—257° (Found: C, 79·1; H, 4·3. $C_{19}H_{12}O_3$ requires C, 79·0; H, 4·2%), separated as a greenish-yellow powder when a solution of (7) (0·5 g.) in acetic anhydride (10 c.c.), which had been treated with hydriodic acid (*d* 1·7; 10 c.c.), and heated under reflux for 3 hours, was poured into aqueous sodium hydrogen sulphite solution. 2′-*Acetoxy*-6 : 7-*benzoflavone* [from (8) with acetic anhydride–pyridine] had m. p. (alcohol) 136—138° (Found: C, 76·8; H, 4·5. $C_{21}H_{14}O_4$ requires C, 76·4; H, 4·2%). Treatment of (7) with alcoholic sodium ethoxide as described above for (6), gave 2-hydroxy-3-acetonaphthone and 2-hydroxy-3-naphthoic acid.

2-2′-*Naphthyl*-6 : 7-*benzochromone*, m. p. (acetone) 193° (Found: C, 85·7; H, 4·9. $C_{23}H_{14}O_2$ requires C, 85·8; H, 4·3%), was obtained from (3) in yellowish plates by treatment with hydriodic acid in acetic anhydride as described for (6).

2-(1′-*Methoxy*-2′-*naphthyl*)-7 : 8-*benzochromone* (9), m. p. (alcohol) 151—152° (Found: C, 81·7; H, 4·7. $C_{24}H_{16}O_3$ requires C, 81·8; H, 4·5%), which separated as a gel from a solution of (4) in warm glacial acetic acid containing hydrogen bromide which had been kept for 1 hour, solidified when the mixture was diluted with water. (9) was also obtained from (4) by the action of cold hydriodic acid in acetic anhydride during 12 hours. Demethylation of (9) with hydriodic acid as described for (7) yielded 2-(1′-*hydroxy*-2′-*naphthyl*)-7 : 8-*benzochromone* as a greenish-yellow powder, m. p. (chlorobenzene) above 280° (Found: C, 81·5; H, 4·2. $C_{23}H_{14}O_3$ requires C, 81·7; H, 4·1%); the *acetyl* derivative had m. p. (alcohol) 174° (Found: C, 79·2; H, 4·4. $C_{25}H_{16}O_4$ requires C, 78·9; H, 4·2%).

2-(3′-*Methoxy*-2′-*naphthyl*)-5 : 6-*benzochromone* or 2-(2′-*methoxy*-1′-*naphthyl*)-6 : 7-*benzochromone* (the latter formula is preferred), m. p. (absolute alcohol–benzene after frequent recrystallisation with addition of charcoal) 197° (Found: C, 81·6; H, 4·7. $C_{24}H_{16}O_3$ requires C, 81·8; H, 4·5%), was isolated in poor yield on treatment of (5) with hydriodic acid in acetic anhydride at 100° for 15 minutes. A better yield was obtained by the action of hydrogen bromide in acetic acid for 12 hours at room temperature. Demethylation with hydriodic acid as described for (7) gave the 2-(*hydroxynaphthyl*)*benzochromone* as a greenish-yellow powder, with m. p. (nitrobenzene) 283—285° (Found: C, 81·6; H, 4·3. $C_{23}H_{14}O_3$ requires C, 81·7; H, 4·1%); the *acetoxy*-compound had m. p. (alcohol) 148—150° (Found: C, 78·6; H, 4·2. $C_{25}H_{16}O_4$ requires C, 78·9; H, 4·2%).

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