404. *Chalkones. Synthesis of* 1-p-*Alkoxyarylidene*-5 : 6-*benzocoumaran*-2-*ones.*

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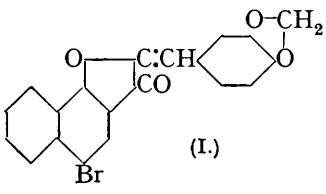
1-Hydroxy-2-naphthyl *p*-alkoxystyryl ketone dibromides, which normally yield flavones with alcoholic alkali, give β-alkoxy-compounds and then arylidenecoumaranones, if the solubility of the dibromide in alcohols is increased by addition of chloroform. With aqueous alkali and acetone the dibromides give the corresponding naphthaflavones (cf. Nadkarni *et al.*, J., 1937, 1798).

NADKARNI, WARRIAR, and WHEELER (J., 1937, 1800) pointed out that the production of benzylidenecoumaran-2-ones in place of flavones from *o*-hydroxy- or *o*-acetoxy-phenyl *p*-alkoxystyryl ketone dibromides by the action of alcoholic alkali probably depends on whether or no the β-bromine atom is first replaced by alkoxyl; it is known that such β-alkoxy-compounds are produced by the action of alcohol on the dibromides of aryl *p*-alkoxystyryl ketones (see Dodwadmath and Wheeler, *Proc. Indian Acad. Sci.*, 1935, **2**, 438). An apparent exception to this view is afforded by 1-acetoxy-2-naphthyl 3 : 4-methylenedioxystyryl ketone dibromide, which yields the corresponding flavone with hot alcoholic alkali (Kostanecki, *Ber.*, 1898, **31**, 708). Experiments with 4-*bromo*-1-*hydroxy*-2-*naphthyl* αβ-*dibromo*-β-3 : 4-*methylenedioxyphenylethyl ketone* have now shown that the flavone is obtained because the relative insolubility of the dibromide in alcohol hinders the formation of a β-ethoxy-compound; the addition of chloroform, which increases the solubility of the dibromide (in alcohol), leads to the production of the *ethoxy*-compound, which with alkali gives 4-bromo-1-piperonylidene-5 : 6-benzocoumaran-2-one (I), apparently the compound obtained by Ullmann (*Ber.*, 1897, **30**, 1466), who, however, gives no melting point. This new method for the production of compounds like (I) has an advantage over that of Ingham, Stephen, and Timpe (J., 1931, 895), who prepare the benzocoumaranone by cyclising the α-naphthyloxyacetyl chloride, in that their method gives an ambiguous result; ring closure can occur in either the 2- or the 8-position. 4-*Bromo*-1-*anisylidene*-5 : 6-*benzocoumaran*-2-*one* was obtained similarly.



(I.)

EXPERIMENTAL.

4-*Bromo*-1-*hydroxy*-2-*naphthyl* αβ-*dibromo*-β-3 : 4-*methylenedioxyphenylethyl ketone*, obtained by treating at 0° a suspension of 1-hydroxy-2-naphthyl 3 : 4-methylenedioxystyryl ketone (6·2 g.) (Kostanecki, *loc. cit.*) in carbon disulphide (150 c.c.) with a solution of bromine (6·2 g.) in carbon disulphide (100 c.c.) and evaporating the solvent after 12 hours, had m. p. 173° after crystallisation from chloroform–light petroleum (Found: Br, 43·5. $C_{20}H_{13}O_4Br_3$ requires Br, 43·1%). The position of the nuclear bromine atom is discussed below.

4-*Bromo*-1-*hydroxy*-2-*naphthyl* α-*bromo*-β-*ethoxy*-β-3 : 4-*methylenedioxyphenylethyl ketone*. Evaporation of the solvent from a mixture of the above dibromide (5 g.), chloroform (100 c.c.), and ethyl alcohol (60 c.c.) which had been heated under reflux for 12 hours gave a residue, m. p. 169—171° after crystallisation from alcohol–chloroform (Found: Br, 30·3. $C_{22}H_{18}O_5Br_2$ requires Br, 30·7%).

4-*Bromo*-1-*hydroxy*-2-*naphthyl* α-*bromo*-β-*methoxy*-β-3 : 4-*methylenedioxyphenylethyl ketone*, which, when crystallised from acetone–alcohol, had m. p. 169—170°, was similarly prepared from the dibromide by means of methyl alcohol (Found: Br, 31·0. $C_{21}H_{16}O_5Br_2$ requires Br, 31·5%).

6-*Bromo*-3' : 4'-*methylenedioxy*-α-*naphthaflavone* separated from a mixture of aqueous potassium hydroxide (10%; 30 c.c.) and 4-bromo-1-hydroxy-2-naphthyl αβ-dibromo-β-3 : 4-methylenedioxyphenylethyl ketone (3 g.) dissolved in acetone (cf. Nadkarni *et al.*, *loc. cit.*) which had been heated under reflux for 5 minutes and cooled. It had m. p. 276° after crystallisation from acetic acid (Found: Br, 20·5. $C_{20}H_{11}O_4Br$ requires Br, 20·3%), and gave a yellow coloration with sulphuric acid.

4-Bromo-1-piperonylidene-5 : 6-benzocoumaran-2-one (I) (cf. Ullmann, *loc. cit.*) separated

from a mixture of alcoholic sodium hydroxide (10%; 10 c.c.), 4-bromo-1-hydroxy-2-naphthyl α-bromo-β-ethoxy-β-3 : 4-methylenedioxyphenylethyl ketone (0·5 g.), and acetone which had been heated under reflux for 5 minutes; it had m. p. 242—243° after crystallisation from nitrobenzene–acetone (Found : C, 60·6; H, 3·3; Br, 20·7. Calc. for $C_{20}H_{11}O_4Br$: C, 60·7; H, 2·8; Br, 20·3%). It gave a deep red coloration with sulphuric acid.

4-Bromo-1-hydroxy-2-naphthyl αβ-dibromo-β-p-anisylethyl ketone (4 g.), which was obtained by treating at 0° a suspension of 1-hydroxy-2-naphthyl *p*-methoxystyryl ketone (4 g.) (Keller and Kostanecki, *Ber.*, 1899, **32**, 1035) in carbon disulphide (150 c.c.) with a solution of bromine (4 g.) in carbon disulphide (100 c.c.) and evaporating the solvent after 12 hours, had m. p. 157—158° after crystallisation from carbon tetrachloride (Found : Br, 44·5. $C_{20}H_{15}O_3Br_3$ requires Br, 44·2%). The position of the nuclear bromine atom in the above compound, and in the corresponding methylenedioxy-dibromide already described, was established as follows :—

4-Bromo-1-hydroxy-2-naphthyl p-methoxystyryl ketone (3 g.), which separated from a mixture of 4-bromo-2-acetyl-1-naphthol (10 g.), alcohol (150 g.) and anisaldehyde (5 g.) which had been treated with aqueous sodium hydroxide (50%; 20 g.), heated at 80° for 2 hours, kept for 12 hours, and diluted with water, had m. p. 184° after crystallisation from acetic acid (Found : Br, 21·3. $C_{20}H_{15}O_3Br$ requires Br, 20·9%). A suspension of the above bromo-chalkone (1·6 g.) in carbon disulphide (50 c.c.), which had been treated at 0° with bromine (0·8 g.) in carbon disulphide (30 c.c.) and kept for 12 hours, gave, on evaporation of the solution, a residue, which, when crystallised from carbon tetrachloride, did not depress the m. p. of the product obtained by direct bromination of 1-hydroxy-2-naphthyl *p*-methoxystyryl ketone as described above. *4-Bromo-1-hydroxy-2-naphthyl α-bromo-β-ethoxy-β-p-anisylethyl ketone* (2·5 g.) remained as a residue when the solvent had been evaporated from a mixture of the corresponding dibromide (5 g.), chloroform (100 c.c.), and ethyl alcohol (70 c.c.) which had been heated under reflux for 12 hours. It had m. p. 155—156° after crystallisation from acetone–alcohol (Found : Br, 31·8. $C_{22}H_{20}O_4Br_2$ requires Br, 31·5%).

4-Bromo-1-hydroxy-2-naphthyl α-bromo-β-methoxy-β-p-anisylethyl ketone, similarly prepared by means of methyl alcohol, had m. p. 146—147° after crystallisation from acetone–alcohol (Found : Br, 32·7. $C_{21}H_{18}O_4Br_2$ requires Br, 32·4%).

6-Bromo-4′-methoxy-α-naphthaflavone (0·8 g.) separated from a mixture of aqueous sodium hydroxide (10%; 20 c.c.) and 4-bromo-1-hydroxy-2-naphthyl αβ-dibromo-β-*p*-anisylethyl ketone (2 g.) in acetone, which had been refluxed for 5 minutes. It had, after crystallisation from acetic acid, m. p. 240—241° (Found : Br, 20·8. $C_{20}H_{13}O_3Br$ requires Br, 21·0%). It gave a yellow colour and green fluorescence with sulphuric acid.

4-Bromo-1-anisylidene-5 : 6-benzocoumaran-2-one (1·4 g.), which separated from a mixture of aqueous sodium hydroxide (10%; 30 c.c.) and 4-bromo-1-hydroxy-2-naphthyl α-bromo-β-methoxy-β-*p*-anisylethyl ketone (2·8 g.) in acetone which had been heated under reflux for 5 minutes, had m. p. 219—220° after crystallisation from chloroform–alcohol (Found : Br, 21·4. $C_{20}H_{13}O_3Br$ requires Br, 21·0%). It gave a deep red coloration with sulphuric acid.

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