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CHALCONE DIHALIDES—IV[1]

STERIC EFFECTS IN THE CYCLIZATION OF 2'-ACETOXY-6'-METHOXYL DERIVATIVES

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Abstract—2'-Acetoxychalcone dibromides and dichlorides having a substituent in the 6'-position were found to form flavones as their major product on cyclization in basic medium. Aurones, the minor products from these reactions, were obtained in significant yields only when substituents were present in *both* the 3'- and 6'-positions. α-Halogenochalcone, a previously proposed intermediate in the formation of aurones, has been prepared and found to form the same products in approximately the same proportions as the corresponding chalcone dihalide.

2'-Hydroxy (or acetoxy) chalcone dihalides (1) may be divided into two classes by considering the products they form in the Emilewicz–von Kostanecki reaction:[2] (1) those that yield only flavones on cyclization with aqueous alcoholic alkali and (2) those that yield aurones under these conditions. Class 2 may be subdivided into three groups as follows: (2A) those with a 6'-OMe substituent in the A-ring, (2B) those having a 2- or 4-alkoxyl group in the B-ring, and (2C) those with a 2- or 4-nitro group in the B-ring.

Members of class 1 are believed[3] to be mechanistically orthodox in their mode of cyclization, the phenoxide anion displacing halide ion from the β-position to form a 3-halogenoflavanone (2) which then eliminates hydrogen halide to form the flavone. The cyclizations of chalcone dihalides of class 2 are of considerable importance as many naturally occurring flavones and aurones are substituted in a manner characteristic of this group. Obviously, however, they are mechanistically more involved as can be seen from the fact that the electronically dissimilar substituents, methoxyl[3,4] and nitro,[1,4] in the 4-position of ring-B, both cause aurone formation. In this paper, the cyclization of chalcone dihalides of group 2A, *i.e.* those whose A-rings have a 6'-OMe substituent, will be considered.

Previously known[4,5] members of this group are chalcone dibromide derivatives of phloracetophenone (e.g. 4, X = Br) and have been found to yield aurones (e.g. 7), exclusively. The parent chalcone, without a nuclear bromine atom, 2'-hydroxy-4',6'-dimethoxychalcone, also yields aurone when treated with alkaline hydrogen peroxide[6] (the Algar-Flynn-Oyamada (AFO) reaction[7]). Geissman and Fukushima[8] have advanced two possible causes for this; firstly, the steric effect of the 6'-OMe substituent reduces conjugation between the A-ring and the CO group making the α-H considerably more acidic and secondly, this substituent offers more steric hindrance to the formation of an adjacent 6-membered ring than it does to the formation of a 5-membered ring. These workers noted the similarity between the AFO and the Emilewicz–von Kostanecki reactions.

The latter explanation, when applied to the cyclization of chalcone dihalides, was considerably strengthened by the later discovery[10] that the nuclear halogen atom, always present in these chalcone dihalides, is not in the 5'-position as supposed,[9] but is, in fact, in the 3'-position, i.e. in the other position *ortho* to the future heterocyclic ring.

We have examined the cyclization products of a series of chalcone dihalides (bromides and chlorides), the 3'- and 6'-substituents of which offer increasing hindrance to heterocyclic ring-formation. The dihalides are: 2'-acetoxy-3',5'-dibromochalcone dihalide (3, X = Hal), 2'-acetoxy-6'-methoxychalcone dihalide (4, X = Hal), 2'-acetoxy-3'-bromo-6'-methoxychalcone dihalide (5, X = Hal), and the previously studied[1] 2'-acetoxy-3'-bromo-4',6'-dimethoxychalcone dihalide (6, X = Hal). 2'-Acetoxy-, rather than the simpler 2'-hydroxy-, chalcone dihalides were employed in the series because the acetoxyl group of 2'-acetoxy-6'-methoxychalcone was vital for the prevention of nuclear halogenation during the conversion of the chalcone to its dihalide (4, X = Hal). It would have been desirable to examine 2'-acetoxy-4',6'-dimethoxychalcone dihalide but, even with the acetoxyl group present, nuclear substitution occurred during the halogenation of the corresponding chalcone. The use of the nuclear dibrominated chalcone dihalide (3, X = Hal) rather than the more suitable nuclear monobrominated compound, 2'-acetoxy-3'-bromochalcone dihalide,

was necessitated by the unavailability, at the time, of the latter's precursor, 3'-bromo-2'-hydroxyacetophenone.[11]

The cyclization reactions were carried out by the addition of 0·2 M KOH to an ethanolic solution or suspension of the chalcone dihalide. The mixture was maintained at 30° for 6 hr and the product composition of the neutral fraction* was established by UV spectroscopy.[12] The results are given in Table 1.

Surprisingly, 2'-acetoxy-3'-bromo-4',6'-dimethoxychalcone dihalide (6, X = Hal), previously considered[2] to give aurone only, not alone gave flavone (8) but gave it as the major product. The failure*[2] of previous workers to isolate the flavone (8) was undoubtedly due to the fact that it is considerably more soluble than the aurone (7) in the solvents commonly used for crystallisation.

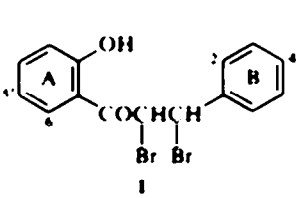
Despite its effectiveness in altering the course of the AFO reaction*[1] the 6'-OMe group alone was highly ineffective in altering the normal course of the present reaction. 2'-Acetoxy-6'-methoxychalcone dihalide (4, X = Hal) gave only a 1–3% yield of 4-methoxyaurone (11). The other substituent *ortho* to the potential heterocyclic ring, the 3'-bromo substituent, was also ineffective – no aurone (9) being formed by the ring closure of 2'-acetoxy-3',5'-dibromochalcone dihalide (3, X = Hal). However, when both "*ortho*" substituents were present, they proved to be reasonably effective in bringing about aurone formation. 2'-Acetoxy-3'-bromo-6'-methoxychalcone dibromide (5, X = Br) gave a 12% yield of 7-bromo-4-methoxyaurone (13) while the corresponding

*For the preliminary note[11] this was established using column chromatography which, as then mentioned, was not satisfactory.

Table 1. Cyclization of chalcone dihalides and α-halogenochalcones

Products	Substrate	Yield (%)	A/F*	Substrate	Yield (%)	A/F*
5,7-Dibromoaurone (9)		0·0			0·0	
	3, X = Br		0·00	3, X = Cl		0·00
6,8-Dibromoflavone (10)		58·5			35·4	
4-Methoxyaurone (11)		1·4			2·9	
	4, X = Br		0·01	4, X = Cl		0·03
5-Methoxyflavone (12)		98·2			95·4	
7-Bromo-4-methoxyaurone (13)		12·3			17·9	
	5, X = Br		0·29	5, X = Cl		0·43
8-Bromo-5-methoxyflavone (14)		43·1			41·2	
7-Bromo-4,6-dimethoxyaurone (7)		20·1			20·6	
	6, X = Br		0·47	6, X = Cl		0·46
8-Bromo-5,7-dimethoxyflavone (8)		42·4			44·4	
7-Bromo-4,6-dimethoxyaurone (7)		18·3			18·9	
	15, X = Br		0·38	15, X = Cl		0·41
8-Bromo-5,7-dimethoxyflavone (8)		48·6			45·7	

*Ratio of aurone to flavone.



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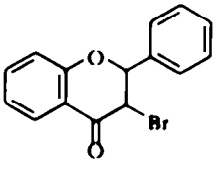

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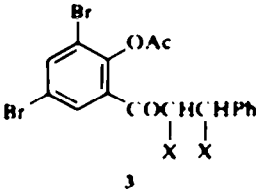

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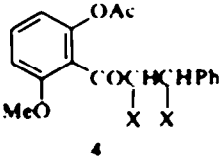

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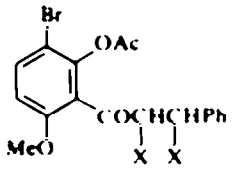

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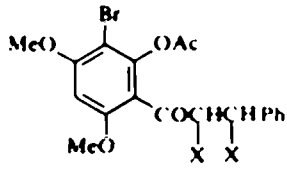

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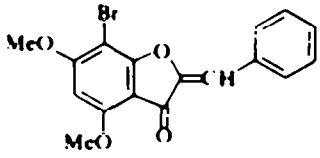

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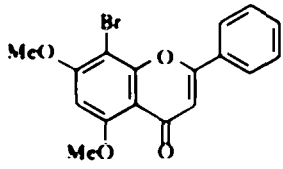

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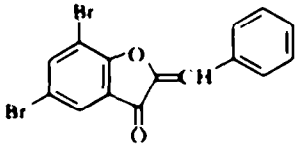

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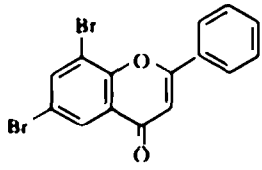

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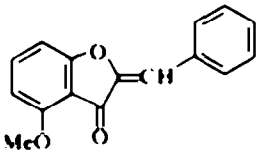

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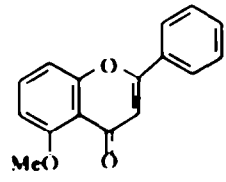

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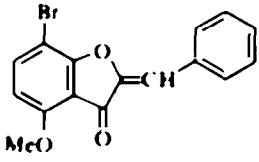

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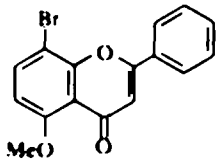

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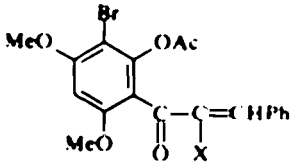
chalcone dichloride (5, X = Cl) gave the relatively high aurone yield of 18%.†

It would appear from these results that the ortho steric effect plays a large part in the formation of aurones from group 2A chalcone dihalides. It may not, however, be the sole cause as the 8% increase in the yield of aurone on introducing a 4'-OMe group into 2'-acetoxy-3'-bromo-6'-methoxychalcone dibromide (5, X = Br) appears too large to be due simply to a buttressing effect by this group on the 3'-bromo substituent of 2'-acetoxy-3'-bromo-4',6'-dimethoxychalcone dibromide (6, X = Br).

While the details of the reaction mechanism(s) for the cyclization of this class of chalcone dihalides must await the synthesis and study of the corresponding series of 2'-hydroxychalcone dihalides, with and without a 3'-bromo substituent, a study of a proposed intermediate was carried out.

von Kostanecki and Tambor,[7] on brominating 2'-

†This could be related to an anomaly of the chalcone dichloride – its NMR spectrum showed it to be a mixture (63:37, approx) of erythro and threo isomers, the other dihalides were single isomers.



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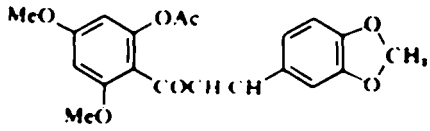

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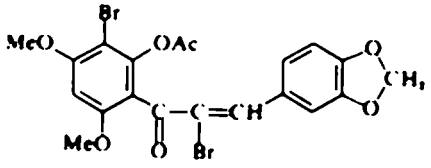

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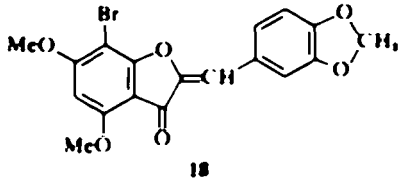

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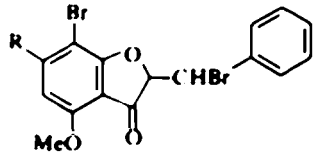

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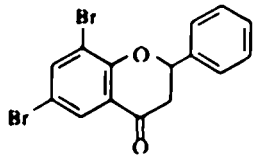

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acetoxy-4',6'-dimethoxy-3,4-methylenedioxychalcone (16), obtained not the chalcone dibromide but the α-bromochalcone (17). This, when cyclized with aqueous ethanolic potassium hydroxide, gave the corresponding aurone (18). As a consequence, α-bromochalcones have often been proposed[3,6,7,15] as intermediates in the formation of aurones from chalcone dibromides of group 2A. Although the analogy between von Kostanecki and Tambor's compound and typical group 2A chalcone dihalides is false,* it is still as likely that aurone formation from these dihalides occurs through an α-halogenochalcone as through the alternative aurone hydrobromide[1] (19) because the steric inhibition of resonance between the aromatic nucleus and the CO group, caused by the *ortho* substituents, enhances the acidity of the α-H and facilitates the elimination of hydrogen halide from the side-chain. It would not be expected, however, that in the cyclization step the intramolecular Michael-type addition of the phenoxide ion would occur at the α-carbon of the double bond.

We have found that the α-bromo (15, X = Br) and α-chloro (15, X = Cl) derivatives of 2'-acetoxy-3'-bromo-4',6'-dimethoxychalcone can readily be prepared by treating the corresponding chalcone dihalide with ethanolic potassium acetate. The NMR spectra of these α-halogeno-chalcones show that they are mixtures of *cis* and *trans* isomers[16] in approximately equal amounts. They could not be separated, however, either by preparative layer chromatography or by fractional crystallisation. When cyclized with aqueous ethanolic potassium hydroxide they yielded (Table 1) aurone in amounts comparable to those obtained from the corresponding chalcone dihalides – so supporting their intermediacy in the cyclization of the latter.

The UV spectroscopic data for the flavone and aurone products are given in Table 2. The standard samples were obtained as follows. Treatment of a suspension of 3'-bromo-2'-hydroxy-4',6'-dimethoxychalcone dibromide in ethanol with aqueous potassium hydroxide gave a mixture of 8-bromo-5,7-dimethoxyflavone (8) and 7-bromo-4,6-dimethoxyaurone (7) which was separated by column chromatography. Similarly, 8-bromo-5-methoxyflavone (14) and 7-bromo-4-methoxyaurone (13) were prepared from 2'-acetoxy-3'-bromo-6'-methoxychalcone dibromide (5, X = Br). 5-Methoxyflavone (12) was obtained by the alkaline cyclization of 2'-acetoxy-6'-methoxychalcone dibromide (4, X = Br). Treatment of 2'-hydroxy-6'-methoxychalcone with alkaline hydrogen peroxide gave 4-methoxyaurone[14] (12). Pyrolysis of 2'-acetoxy-3',5'-dibromochalcone dibromide (3, X = Br) under reduced pressure gave 6,8-dibromoflavone (10) together with 6,8-

*It has since been found[4] that a methylenedioxy or similar group on the B-ring greatly increases the leaving group effectiveness of the β-bromine. This chalcone dibromide system of von Kostanecki and Tambor belongs as much to group 2B and to group 2A.

Table 2. UV and visible spectra of flavones and aurones

	λ_{max} (log ε)
8-Bromo-5,7-dimethoxyflavone (**5**)	267 (4·46), 285 s (4·20), 323 (4·09)
6,8-Dibromoflavone (**10**)	261 (4·24), 304 (4·21), 329 (4·14)
5-Methoxyflavone (**12**)	263 (4·41), 290 s (4·12), 320 (4·07)
8-Bromo-5-methoxyflavone (**14**)	267 (4·35), 295 s (4·08), 327 (4·04)
7-Bromo-4,6-dimethoxyaurone (**7**)	246 s (4·18), 314 (4·26), 383 (4·29)
4-Methoxyaurone[17] (**11**)	308 (4·22), 389 (4·34)
7-Bromo-4-methoxyaurone (**13**)	267 s (3·88), 275 s (3·94), 306 (4·18), 394 (4·35)

dibromoflavanone (**20**) and 3',5'-dibromo-2'-hydroxychalcone. The dibromoflavone (**10**) was more easily obtained by the cyclization of the dibromochalcone dibromide (3, X = Br) with potassium hydroxide.

EXPERIMENTAL

UV spectra were taken in $CHCl_3$ using a Unicam SP500 spectrometer. NMR spectra were obtained at 60 MHz with a Perkin Elmer R12 spectrometer, in deutero-$CDCl_3$ with TMS as internal reference. M.ps were taken with a Kofler hot-stage apparatus.

The standard conditions for the cyclization of chalcone dihalides and α-halogeno-chalcones were as follows. EtOH (10 ml) was added to the halide (6.5 × 10^{-3} mol) and the resulting solution or suspension was stirred in a closed tube at 30° for 30 min. 0·2 M KOH (1 ml) was added and stirring continued for 6 hr. Then, 4 min after the addition of water (20 ml), the mixture was extracted with five 10 ml portions of $CHCl_3$. The combined $CHCl_3$ extracts were washed once with water (10 ml) before being diluted for the observation of their UV spectra.

2'-Acetoxy-3'-bromo-4',6'-dimethoxychalcone dihalides (6, X = Hal). Acetylation of 3'-bromo-2'-hydroxy-4',6'-dimethoxychalcone[16] (8·2 g) with Ac_2O and AcONa gave *2'-acetoxy-3'-bromo-4',6'-dimethoxychalcone* (4·5 g), m.p. 187–188° (acetone). (Found: C, 56·7; H, 4·4; Br, 19·3. $C_{19}H_{17}BrO_5$ requires: C, 56·3; H, 4·2; Br, 19·7%).

Addition of bromine (2 g) in CCl_4 (20 ml) to a soln of the acetoxychalcone (5 g) in CCl_4 (150 ml) gave **6** (X = Br, 5·8 g), m.p. 184–186° (lit.[7] m.p. 185°). Similar addition of chlorine (1 g) to the acetoxychalcone (5 g) gave *2'-acetoxy-3'-bromo-2,3-dichloro-4',6'-dimethoxy-3-phenylpropiophenone* (**6**, X = Cl), (3·7 g), m.p. 192–193° (benzene-light petroleum b.p. 40–60°) (Found: C, 47·3; H, 3·6. $C_{19}H_{17}BrCl_2O_5$ requires: C, 47·9; H, 3·6%).

A mixture of **6** (X = Br, 2 g), and AcOK (2·5 g) in EtOH (60 ml) was refluxed for 30 min. *2'-Acetoxy-α,3'-dibromo-4',6'-dimethoxychalcone* (**15**, X = Br) precipitated on cooling and crystallised from aqueous EtOH in prisms (1·6 g), m.p. 168–170° (Found: C, 47·3; H, 3·4; Br, 32·5. $C_{19}H_{16}Br_2O_5$ requires: C, 47·1; H, 3·3; Br, 33·0%). Its NMR spectrum showed it to be an approximately 50:50 mixture of *cis* and *trans* isomers. OAc τ 7·77 and τ 7·67; OMe τ 6·18, τ 6·18, τ 6·10, and τ 6·04; 5'-H τ 3·79 and τ 3·53.

Similarly, **6** (X = Cl, 0·5 g), gave *2'-acetoxy-3'-bromo-α-chloro-4',6'-dimethoxychalcone* (**15**, X = Cl), which crystallised in prisms (0·35 g) from aqueous EtOH, m.p. 168–169° (Found: C, 51·8; H, 3·7; Hal, 26·1. $C_{19}H_{16}BrClO_5$ requires: C, 51·9; H, 3·7; Hal, 26·2%). Its NMR spectrum showed it to be an approximately 50:50 mixture of *cis* and *trans* isomers. OAc τ 7·79 and τ 7·68; OMe τ 6·18, τ 6·18, τ 6·18, τ 6·13, and τ 6·03; 5'-H τ 3·79 and τ 3·53.

40% KOH aq (5 ml) was added to a suspension of 2,3,3'-tribromo-2'-hydroxy-4',6'-dimethoxy-3-phenylpropiophenone (5·2 g) in EtOH (50 ml). After 1 hr, water was added and the ppt was chromatographed on a column of alumina to give **7**, which crystallised from acetone in needles (1·5 g), m.p. 258–259° (lit.[16] m.p. 251°), and **8**, m.p. 256–257° (acetone), (lit.[16] m.p. 250–252°).

2'-Acetoxy-3'-bromo-6'-methoxychalcone dihalides (**5**, X = Hal). Acetylation of 3'-bromo-2'-hydroxy-6'-methoxychalcone[16] (12·3 g) gave its *acetate* (13·9 g), m.p. 119–120° (EtOH) (Found: C, 58·0; H, 3·9; Br, 21·0. $C_{18}H_{15}BrO_5$ requires: C, 57·7; H, 4·0; Br, 21·3%).

Addition of bromine (2·1 g) in CCl_4 (40 ml) to a soln of the acetate (5 g) in CCl_4 (50 ml) gave *2'-acetoxy-2,3'-tribromo-6'-methoxy-3-phenylpropiophenone* (**5**, X = Br, 5·4 g), m.p. 172° (benzene-light petroleum b.p. 60–80°) (Found: C, 40·4; H, 3·0; Br, 44·5. $C_{18}H_{15}Br_3O_5$ requires: C, 40·4; H, 2·8; Br, 44·8%). Similarly, addition of chlorine (1·3 g) to the acetate (6 g) gave *2'-acetoxy-3'-bromo-2,3-dichloro-6'-methoxy-3-phenylpropiophenone* (**5**, X = Cl, 4 g), m.p. 145–147° (ligroin) (Found: C, 48·6; H, 3·4; Hal, 33·4. $C_{18}H_{15}BrCl_2O_5$ requires: C, 48·5; H, 3·4; Hal, 33·8%). Its NMR spectrum showed it to be a mixture (63:37, approx.) of erythro and threo isomers; erythro, H_α τ 4·36, H_β τ 4·62, $J_{\alpha\beta}$ 6·7 Hz, threo isomer, H_α and H_β, τ 4·63.

20% KOH aq (5·5 ml) was added to a suspension of **5** (X = Br, 2·5 g), in EtOH (65 ml). After 1 hr, the mixture was diluted with water and the ppt was chromatographed on alumina to give **7** *bromo-4-methoxyaurone* (**13**), which crystallised from i-PrOH in yellow needles (0·54 g), m.p. 202–203° (Found: C, 58·1; H, 3·3. $C_{16}H_{11}BrO_3$ requires: C, 58·0; H, 3·4%), and **14** (0·72 g), m.p. 192–193° (i-PrOH), (lit.[16] m.p. 190–192°).

2'-Acetoxy-6'-methoxychalcone dihalides (**4**, X = Hal). Acetylation of 2'-hydroxy-6'-methoxychalcone[16] (7·7 g) gave the *acetate* (6·3 g) as a glass (Found: C, 72·6; H, 5·7. $C_{18}H_{16}O_5$ requires: C, 73·0; H, 5·5%).

Bromine (2·9 g) in CCl_4 (60 ml) was added slowly to a soln of the acetoxychalcone (5·0 g) in CCl_4 (500 ml). Evaporation of the solvent gave *2'-acetoxy-2,3-dibromo-6'-methoxy-3-phenylpropiophenone* (**4**, X = Br) which crystallised from benzene-light petroleum (b.p. 60–80°) in prisms (5·3 g), m.p. 142–143° (Found: C, 47·4; H, 3·6; Br, 35·1. $C_{18}H_{16}Br_2O_5$ requires: C, 47·4; H, 3·6; Br, 35·4%). Addition of Cl_2 (1·1 g) to the acetoxychalcone (4·2 g) gave *2'-acetoxy-2,3-dichloro-6'-methoxy-3-phenylpropiophenone* (**4**, X = Cl), prisms (3·5 g) from

benzene–light petroleum (b.p. 60–80°), m.p. 121–122°. (Found: C, 59.3; H, 4.6; Cl, 20.3. $C_{16}H_{14}Cl_4O_4$ requires: C, 58.9; H, 4.4; Cl, 19.3%)

Addition of 20% KOH aq. (7 ml) to a soln of **4** (X = Br; 2.5 g), in EtOH (100 ml), followed, 1 hr later, by dilution with water gave 5-methoxyflavone which crystallised in needles (0.85 g) from i-PrOH, m.p. 130° (lit.[19] m.p. 131–132°).

2'-Acetoxy-3',5'-dibromochalcone dihalides (**3**, X = Hal). Br_2 (2.85 g) in $CHCl_3$ (20 ml) was added to a soln of 2'-acetoxy-3',5'-dibromochalcone[20] (7.5 g) in $CHCl_3$ (100 ml). The product, *2'-acetoxy-2,3,3',5'-tetrabromo-3-phenylpropiophenone* (**3**, X = Br; 5.1 g), crystallised from ligroin, m.p. 146° (Found: 35.0; H, 2.0; Br, 54.8. $C_{17}H_{12}Br_4O_3$ requires: C, 35.4; H, 2.1; Br, 54.4%). Similar addition of Cl_2 (0.53 g) to the acetoxychalcone (3.0 g) gave *2'-acetoxy-3',5'-dibromo-2,3-dichloro-3-phenylpropiophenone* (**3**, X = Cl) which crystallised from ligroin in prisms (1.9 g), m.p. 112–113° (Found: C, 40.8; H, 2.4; Hal, 46.7. $C_{17}H_{12}Br_2Cl_2O_3$ requires: C, 41.2; H, 2.4; Hal, 46.6%).

Compound **3** (X = Br; 300 mg) was heated at 180°/20 mm for 3 hr. The product was separated by preparative layer chromatography on silica gel into three components: 3',5'-dibromo-2'-hydroxychalcone (18 mg), m.p. 143–144° (lit.[20] m.p. 145°), 6,8-dibromoflavanone (43 mg), m.p. 138–139° (lit.[20] m.p. 140°), and **10**, (58 mg), m.p. 174–175° (lit.[20] m.p. 166°). Compound **10**, (90 mg), was also prepared by the addition of 15% KoH aq. (1 ml) to a suspension of **3** (X = Br; 300 mg), in EtOH (5 ml). It crystallised from light petroleum (b.p. 80–100°) in needles, m.p. 174–175°.

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