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α-HALOGENOKETONES—XIII[1]

CHROMONE EPOXIDES; THEIR SYNTHESIS AND ACID-CATALYSED REARRANGEMENT

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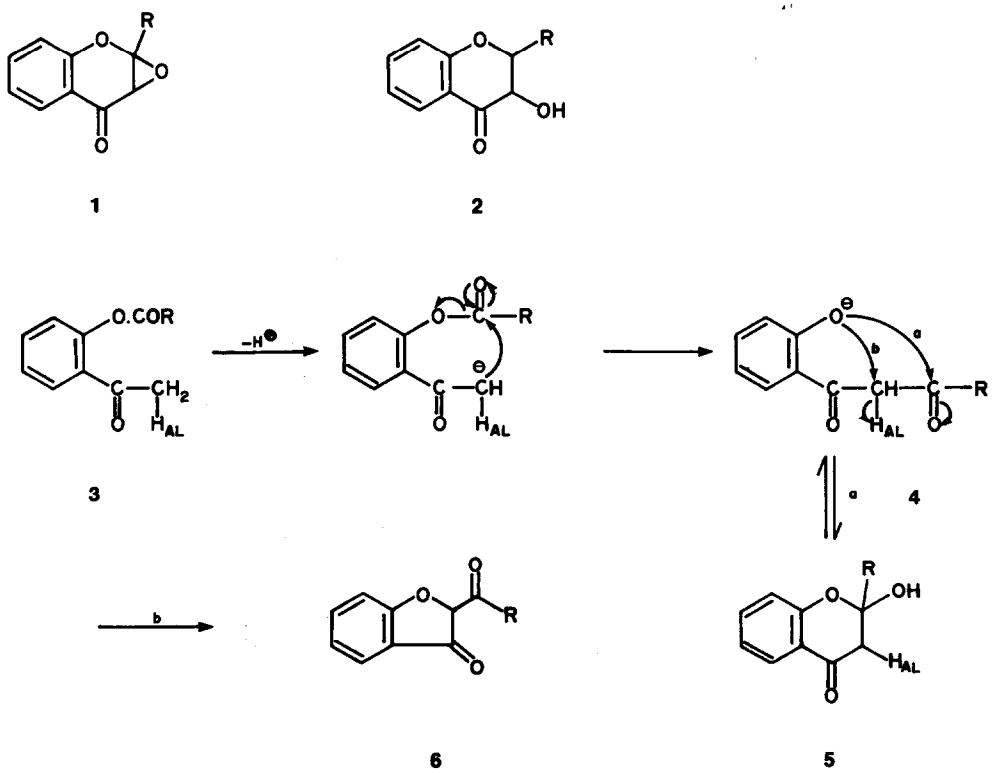
Abstract—The chromone epoxide ring system has been synthesised. Base-catalysed cyclization and dehydrobromination of α-bromo-o-acyl (aroyl) oxyacetopheones or 2-bromo-1, 3-diones yielded 3-substituted chromone epoxides. Acid-catalysed rearrangement of a 2-methylchromone epoxide in an aprotic solvent gave a 2-methylenechromanonol, while a 3-methoxymethylchromone epoxide fragmented to chromonol under these conditions; in alchols, chromone epoxides gave 2-alkoxychromanonols.

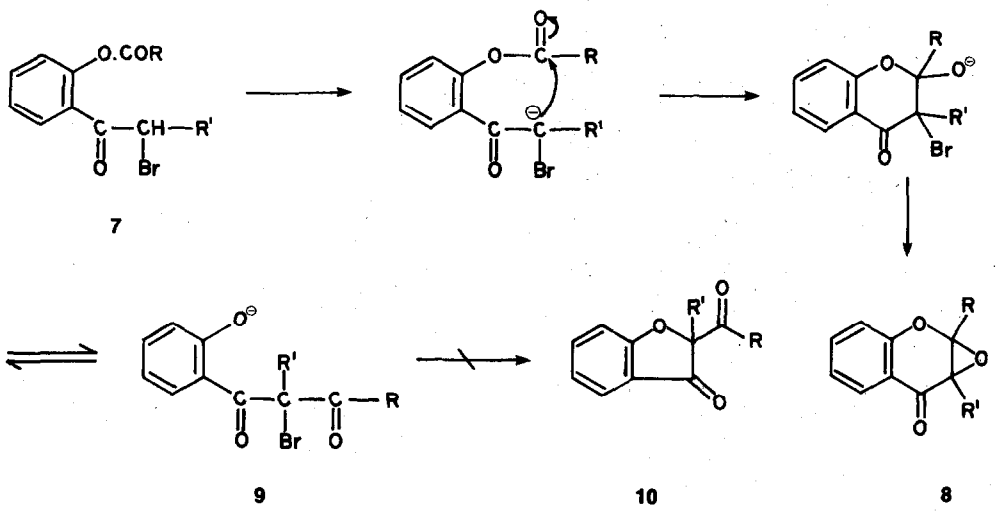
It has not been found possible to locate in the literature the synthesis or isolation of a chromone epoxide **1**, in spite of the importance of the 3-hydroxy-chromone and chromanone **2** systems in flavonoid chemistry. Perhaps the difficulty of converting flavone into its epoxide (**1**; R = Ph) has discouraged attempts to prepare these potentially useful intermediates.

It has now been found[2] that chromone epoxides can be obtained by the base-catalysed rearrangement, with elimination of hydrogen bromide, of *secondary* halogeno α-bromo-*o*-acyl(aroyl) oxyacetophenones—a reaction which contrasts with that of primary halogeno α-chloro-*o*-acyl(aroyl) acetophenones **3**, long known[3] to produce 2-acyl(aroyl)-3-coumaranones **6**. The latter is the Auwers coumaranone synthesis and has been shown[4] to involve (Scheme 1) an initial Baker–Venkataraman transformation of an ester **3** into a 2-halogeno-1, 3-diketone **4** which, though in equilibrium with a chromone *haloydrin* **5**, as shown by Obara and Onodera,[5] eliminates hydrogen halide to form a 2-acyl(aroyl)-3-coumaranone **6**. α-Bromo-acetophenones undergo[6] the Auwers reaction just as readily as their α-chloro analogues.

The formation of chromone epoxides **8** by α-bromo-acetophenones **7** probably occurs by an intramolecular Darzens reaction (Scheme 2) resembling the conversion of 1, 4-dibenzoyl-1, 4-dibromobutane **11** into 2-benzoyl-5-bromo-1-phenylcyclopentene oxide **12** observed[7] by Wasserman and Gorbunoff. The concurrent production of a 2-bromo-1, 3-diketone **9** by a Baker-Venkataraman rearrangement is also likely but the difficulty of substitut-



Scheme 1.

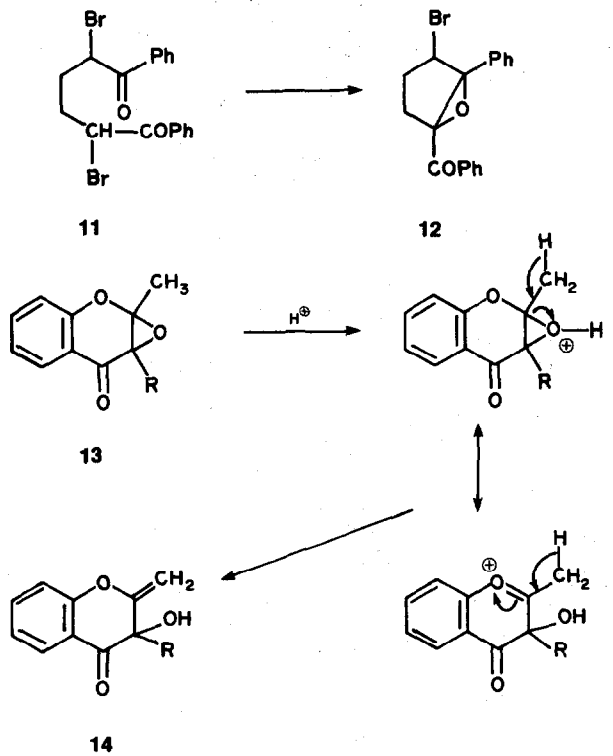


Scheme 2.

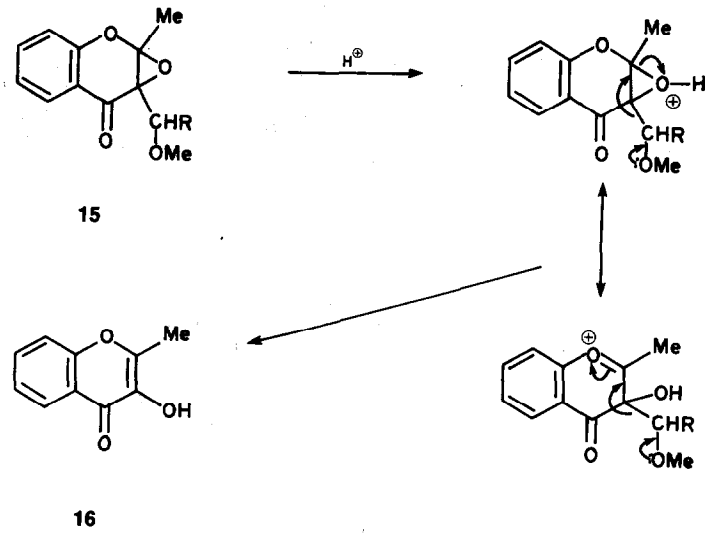
ing a tertiary α-bromo ketone presumably prevents the diketone **9** cyclizing to a 3-coumaranone **10**. It has since been observed,[8] incidently, that chromones and isoflavones may be epoxidized by alkaline hydrogen peroxide.

Chromone epoxides **8** having a proton-carrying substituent in the 2-position or an alkoxyl-carrying substituent in the 3-position were found to be more susceptible than others to acid-catalysed reactions in aprotic solvents. Thus, a 2-methyl-substituted chromone epoxide **13** was rearranged (Scheme 3) by p-toluenesulphonic acid (PTSA) in benzene to a 2-methylene-chromanonol **14** but, under the same conditions, a 3-methoxymethyl-2-methylchromone epoxide **15** suffered a fragmentation reaction (Scheme 4) to form a chromonol **16**, a reaction that appears to be typical[9] of 3-methoxymethylchromone epoxides. All chromone epoxides, so far examined, readily underwent acid-catalysed reactions in alcohol, forming 2-alkoxy-chromanonols **17**.

The bromination of 2'-acetoxy-2-phenylacetophenone **18** in acetic acid gave 2'-acetoxy-2-bromo-2-phenylacetophenone **19** which was cyclized smoothly by aqueous methanolic sodium hydroxide to 2-methyl-3-phenyl-chromone epoxide **20**. Support for the chromanone structure of this product rather than the coumaranone structure **21** is provided by the reactions mentioned below and by its sole infrared carbonyl absorption at 1684 cm^{-1} which is more typical of chromanones[10a] (1680 cm^{-1}) than coumaranones[10b] (1705 cm^{-1}). Also, the methyl signal of its ^1H NMR spec-



Scheme 3.



Scheme 4.

trum at 1.66δ is closer to that expected for the chromanone[11a] (>1.32δ) than that expected for the coumaranone[11b] (>2.09δ). Finally, the exceptional deshielding of one aromatic proton at 8.02δ is characteristic of the 5-H of a chromanone and not at all characteristic of the corresponding 4-H of a coumaranone.

2-Methyl-3-phenylchromone epoxide **20** was ring-opened by ethanolic benzene containing a catalytic amount of PTSA and gave both diastereomers of 2-ethoxy-3-hydroxy-2-methyl-3-phenylchromanone **22** in the proportion of 7:3. It may be assumed that the major product results[12] from the common *anti*-opening of epoxides but, if the reaction is substantially assisted by carbocation stabilization by substituents in the 2-position[13] or by the 3-phenyl group[14], it may have the opposite configuration. The acid-catalysed reaction of 2-methyl-3-phenylchromone epoxide **20** in benzene resulted in its rearrangement to 3-hydroxy-2-methylene-3-phenylchromanone **23**.

Acetylation of 2'-hydroxy-4'-methoxy-2-phenylacetophenone, followed by bromination of the resulting acetate **24** in acetic acid, gave 2'-acetoxy-2-bromo-4'-methoxy-2-phenylacetophenone **25**. Treatment of this α-bromoketone with aqueous methanolic sodium hydroxide gave, however, only a poor yield of 7-methoxy-2-methyl-3-phenylchromone epoxide **26**. The corresponding benzoate, 2'-benzoyloxy-2-bromo-4'-methoxy-2-phenylacetophenone **27**, failed to yield any epoxide; conditions for a reasonably clean reaction could not be found. The poor epoxide-forming ability of these two acetophenones may be related to a decrease in the acidity of the sidechain hydrogen caused by the p-methoxyl substituent.

Bromination of 2'-benzoyloxy-2-phenylacetophenone gave 2'-benzoyloxy-2-bromo-2-phenylacetophenone **28** which was cyclized by aqueous methanolic sodium hydroxide to give what could be considered to be a flavone epoxide, 2,3-diphenylchromone epoxide **29**. This epoxide reacted with ethanol containing a trace of PTSA to give but one diastereomer of 2-ethoxy-3-hydroxy-2,3-diphenylchromanone **30**. The substitution of this epoxide by phenyl groups at the 2- and 3-positions makes it likely[13,14] that the product is the result of *syn*-opening. As the mechanism set out above (Scheme 2) for the formation of chromone epoxides **8** from α-bromoacetophenones **7** suggests that tertiary halogeno 2-bromo-1, 3-diketones **9** should likewise yield these epoxides, it was decided to investigate the possibility of preparing 2,3-diphenylchromone epoxide **29** by the dihydrobrominative cyclization of the corresponding 1, 3-diketone.

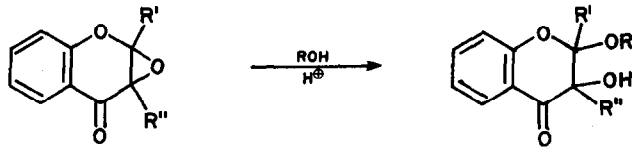
2'-Benzoyloxy-2-phenylacetophenone underwent the Baker–Venkataraman transformation to give 1-(2-hydroxyphenyl)-2, 3-diphenyl-1, 3-propandione **31**. The attempted bromination of this diketone to obtain the required 2-bromo-1, 3-diketone **32** was unsuccessful as it cyclized to 2,3-diphenyl-chromone **33**; presumably the initial bromination of the side-chain of some of the diketone **31** liberated sufficient hydrogen bromide to catalyse the dehydrative cyclization of the remainder. Bromination of the diketone **31** using *N*-bromosuccinimide gave 1-(3, 5-dibromo-2-hydroxyphenyl)-2, 3-diphenyl-1, 3-propandione **34**. However, protection of the 2-hydroxyl group in the diketone **31** by acetylation, followed by bromination of the resulting acetate **35** with bromine in acetic acid gave the acetyl derivative **36** of the required tertiary halogeno 2-bromo-1, 3-diketone **32**. It was found unnecessary to remove the protecting group as this acetate **36** cleanly cyclized to 2, 3-diphenylchromone epoxide **29** on reacting with aqueous methanolic sodium hydroxide. Thus, chromone epoxides are also available from tertiary halogeno 2-bromo-1, 3-diones.

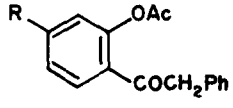
Bromination of 2'-acetoxy-4', 6'-dimethoxy-2-phenylacetophenone **37** in acetic acid resulted in nuclear halogenation, presumably[15] in the 3'-position, and deacetylation to give 3'-bromo-2'-hydroxy-4', 6'-dimethoxy-2-phenylacetophenone **38**. Re-acetylation, followed by bromination of the acetate **39** gave 2'-acetoxy-2, 3'-dibromo-4', 6'-dimethoxy-2-phenylacetophenone **40**. This secondary halogeno α-bromo ketone did not form a chromone epoxide when treated with aqueous methanolic sodium hydroxide. Instead, the 1, 2-diketone, 3-bromo-2-hydroxy-4, 6-dimethoxybenzil **41** was obtained, probably by deacetylation and hydroxide substitution of the bromine to give an easily oxidisable α-ketol **42**.

3-Methoxymethyl-2-methylchromone epoxide[16] **43** reacted with PTSA in benzene to yield, mainly, 2-methylchromonol **44**. Two minor products were also

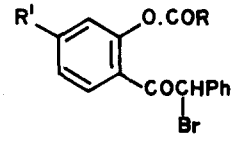
isolated, t-3-hydroxy-r-2-methoxymethyl-3-methoxymethyl-2-methylchromanone **45** and t-3-hydroxy-r-2-methoxy-3-methoxymethyl-2-methylchromanone **46**. These by-products are believed to arise (Scheme 5) by hydration and hydrolysis of the cation fragment of the main reaction by the hydrated PTSA to yield, respectively, methoxymethanol and methanol plus formaldehyde, followed by the acid-catalysed reaction of these alcohols with the chromone epoxide **43**. 3-Methoxymethyl-2-methylchromone epoxide **43** underwent acid-catalysed ring-opening in the presence of ethanol to give almost equal quantities of the two diastereomers of 2-ethoxy-3-hydroxy-3-methoxymethyl-2-methylchromanone **47**.

The lack of stereoselectivity in this reaction precludes the assignment of configuration to the products on that basis. In separate experiments, both diastereomers were found to be stable under these reaction conditions and showed no tendency to interconvert.

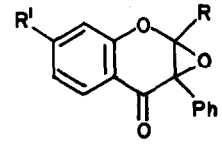




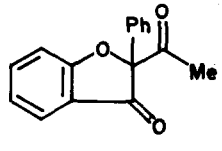
18: R = H
24: R = OMe



19: R = Me, R' = H,
25: R = Me, R' = OMe
27: R = Ph, R' = OMe
28: R = Ph, R' = H



20: R = Me,R' = H
26: R = Me,R' = OMe
29: R = Ph, R' = H



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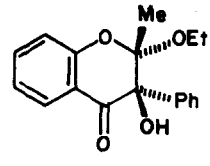

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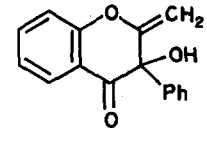

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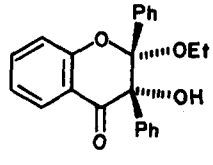

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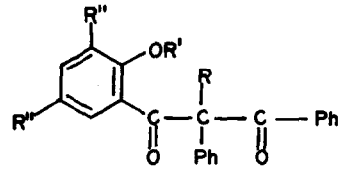
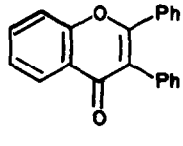
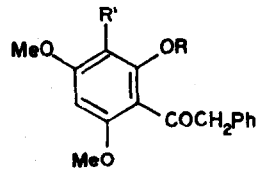


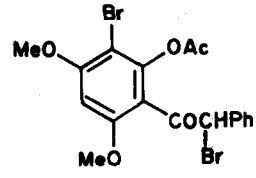


33

31: R = R' = R" = H
32: R = Br, R' = R" = H
34: R = R' = H, R" = Br
35: R = R" = H, R' = Ac
36: R = Br, R' = Ac, R" = H



37: R = Ac, R' = H
38: R = H, R' = Br
39: R = Ac, R' = Br



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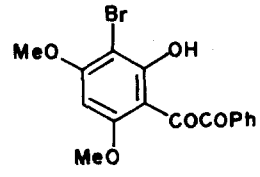

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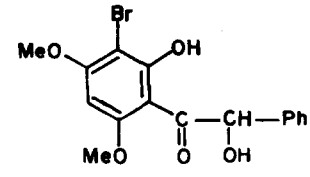

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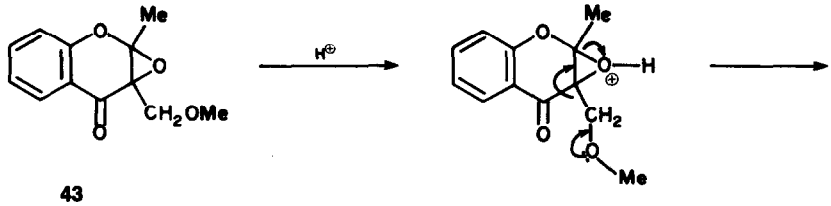

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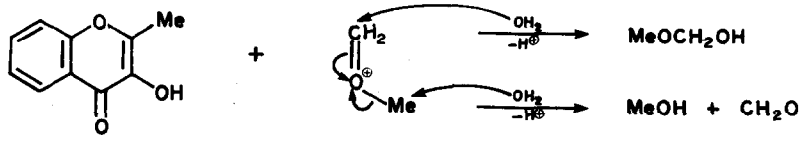

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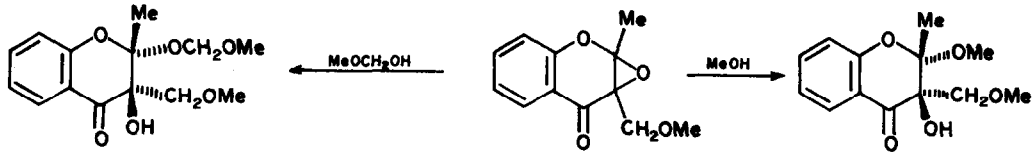

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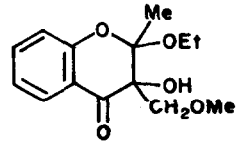

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Scheme 5.

EXPERIMENTAL

^{1}H NMR spectra were obtained at 60 MHz in $CDCl_3$ with TMS as interal reference. Chemical shifts are given in ppm (**6**). Hydroxyl signals were identified by deuteriation. M.ps were taken with a Kofler hot-stage apparatus. Solids were crystallized from ethanol unless otherwise stated. Satisfactory analyses (*C*, ± 0.4; *H*, ± 0.2; *Hal*, ± 0.5%) were obtained for new compounds. The usual work-up consisted of diluting the reaction mixture with water, extracting with chlorform, washing the chloroform extract with water, drying the extract over anhydrous sodium sulphate, removing the solvent, and fractionating the residue by thin layer chromatography (tlc) on silica gel.

2-Methyl-3-phenylchromone epoxide **20**

A solution of 2'-hydroxy-2-phenylacetophenone (5g) in acetic anhydride (15 ml) was heated with sodium acetate (5 g) on a steambath for 1 h cooled, and poured into ice-water. The precipitate crystallized in colourless plates (4.59 g) of 2'-acetoxy-2-phenylacetophenone **18**, m.p. 106–7° NMR: 2.30 (s, OAc), 4.24 (s, CH_2), 7.10–7.95 (m, Ar).

Bromine (1.88 g) in acetic acid (20 ml) was added slowly to a solution of the acetate (3.0 g) in acetic acid (37 ml). After 1 h, the usual work-up (without tlc) gave 2'-acetoxy-2-bromo-2-phenylacetophenone **19** which crystallized in colourless prisms (3.60 g), m.p. 86–8°. NMR: 2.35 (s, OAc), 6.30 (s, CHBr), 7.00–7.85 (m, Ar).

Aqueous sodium hydroxide (0.2 M; 30 ml) was added dropwise to a solution of the bromoacetophenone (1.0 g) in methanol (40 ml). After 1 h and the usual work-up (without tlc), the residue crystallized in colourless plates (0.26 g) of 2-methyl-3-phenylchromone epoxide **20**, m.p. 98–9°. NMR: 1.66 (s, Me), 7.04–8.13 (m, Ar). IR: 1684 cm^{-1} (C = O).

A solution of the chromone epoxide (0.2 g) and PTSA (trace) in dry benzene (15 ml) and ethanol (3 ml) was heated under reflux for 4 h, diluted with benzene, and worked-up as usual, using benzene in place of chloroform. The following products were isolated in order of decreasing R_f values.

r-2-Ethoxy-t-3-hydroxy-2-methyl-3-phenylchromanone **22**, an oil (0.07 g). 0.95 (t. OEt; J7 Hz), 1.51 (s, 2-Me), 3.65 (octet, OEt), 3.92 (s, OH), 6.98-7.80 (m, Ar), 7.96 (q, 5-H; J2 and 8 Hz).

r-2-Ethoxy-c-3-hydroxy-2-methyl-3-phenylchromanone which crystallized in colourless plates (0.03 g) from chloroform-hexane, m.p. 109–110°; NMR: 0.99 (t, OEt; J7 Hz), 1.47 (s, 2-Me), 3.45 (s, OH), 3.65 (q, OEt), 6.98–7.85 (m, Ar), 8.04 (q, 5-H; J2 and 8 Hz).

PTSA (trace) was added to a solution of the chromome epoxide (0.30 g) in dry benzene (15 ml). After 12 h and the usual work-up, using benzene in place of chloroform, 3-hydroxy-2-methylene-3-phenylchromanone **23** was obtained as colourless prisms (0.160 g), m.p. 154–6°. NMR: 4.50 (s, OH), 5.30 (d, 2-CH; J2 Hz), 5.49 (d, 2-CH), 6.70–7.96 (m, Ar).

7-Methoxy-2-methyl-3-phenylchromone epoxide **26**

A solution of 2'-hydroxy-4'-methoxy-2-phenylacetophenone (5.0 g) in acetic anhydride (15 ml) was heated with sodium acetate (5 g) on a steambath for 1 h, cooled, and poured into iced water. The precipitate was crystallized, giving 2'-acetoxy-4'-methoxy-2-phenylacetophenone **24** (4.0 g) m.p. 123–5°. NMR 2.32 (s, OAc), 3.85 (s, OMe), 4.20 (s, CH_2), 6.62–7.92 (m, Ar), 7.30 (s, Ph).

Bromine (1.68 g) in acetic acid (20 ml) was added slowly to a solution of the acetate (3.0 g) in acetic acid (37 ml). After 1 h and the usual work-up (without tlc), the residue was crystallized, giving 2'-acetoxy-2-bromo-4'-methoxy-2-phenylacetophenone **25** (2.38 g), m.p. 82–3°. NMR: 2.39 (s, OAc), 3.86 (s, OMe), 6.35 (s, CHBr), 6.67–7.64 (m, Ar).

Aqueous sodium hydroxide (0.2M; 25 ml) was added dropwise to a solution of the bromacetophenone (1.0 g) in methanol (40 ml). After 1 h and the usual work-up, the product was crystallized, giving, 7-methoxy-2-methyl-3-phenylchromone epoxide **26** (0.08 g), m.p. 129–130°. NMR: 1.66 (s, 2-Me), 3.92 (s, Me), 6.60–8.00 (m, Ar), 7.49 (s, Ph). IR: 1665 cm^{-1} (C = O).

2,3-Diphenylchromone epoxide **29**

Benzoyl chloride (3.19 g) was added to a solution of 2'-hydroxy-4'-methoxy-2-phenylacetophenone (5.0 g) in pyridine (4 ml). After 1 h, the mixture was poured into dilute aqueous hydrochloric acid and worked up as usual (but without tlc). The residue crystallized in colourless plates (4.00 g) of 2'-benzoyloxy-4'-methoxy-2-phenylacetophenone, m.p 85–6°. NMR: 3.85 (s, OMe), 4.20 (s, CH_2), 6.75–8.36 (m, Ar).

Bromine (1.44 g) in acetic acid (20 ml) was added slowly to a solution of the benzoate (3.0 g) in acetic acid (37 ml). After 1 h, and the usual work-up (without tlc), the residue was crystallized, giving, 2'-benzoyloxy-2-bromo-4'-methoxy-2-phenylacetophenone **27** (2.80 g), m.p. 114–6°. NMR: 3.81 (s, OMe), 6.36 (s, CHBr), 6.72–8.30 (m, Ar).

Bromine (1.51 g) in acetic acid (20 ml) was added slowly to a solution of 2'-benzoyloxy-2-phenylacetophenone[17] (3.0 g) in acetic acid (37 ml). After 1 h and the usual work-up (without tlc), the residue was crystallized, giving 2'-benzoyloxy-2-bromo-2-phenylacetophenone **28** in colourless prisms (3.50 g), m.p. 96–8°. NMR: 6.30 (s, CHBr), 7.28–8.26 (m, Ar).

Aqueous sodium hydroxide (0.2M; 25 ml) was added dropwise to a solution of the bromoacetophenone (1.0 g) in methanol (30 ml). After 1 h, the usual work-up gave 2, 3-diphenylchromone epoxide **29** which crystallized in colourless needles (0.20 g), m.p. 128–130°, from benzene–hexane. NMR: 7.15–7.87 (m, Ar), 8.15 (q, 5-H; J3 and 8 Hz). IR: 1680 cm^{-1} (C = O).

Powdered potassium hydroxide (0.56 g) was added to a solution of 2'-benzoyloxy-2-phenylacetophenone (3.16 g) in dry pyridine (20 ml). The reaction mixture was shaken vigorously for 15 min and poured into dilute hydrochloric acid. The usual work-up (with tlc) gave an oil which was crystallized, giving 1-(2-hydroxyphenyl)-2, 3-diphenyl-1, 3-propandione **31** in colourless plates (2.8 g) m.p. 139–142°. NMR: 6.68 (s, CHPh), 6.70–8.10 (m, Ar), 12.00 (s, OH).

Bromine (0.5 g) in carbon tetrachloride (10 ml) was added dropwise to a solution of the 1, 3-dione (1.0 g) in carbon tetrachloride (10 ml) at 0° After 12 h the solvent was removed and the residue crystallized from diethyl ether-hexane in colourless needles (0.70 g) of 2, 3-diphenylchromone **33**, m.p. 148–9° (*lit.*[18] m.p. 152°). A similar result was obtained using acetic acid as solvent.

A solution of the 1, 3-dione (0.5 g) and *N*-bromosuccinimide (0.28 g) in chloroform (10 ml) was refluxed for 7 h. After the usual work-up, the product was crystallized from diethyl ether-hexane, giving 1-(3, 5-dibromo-2-hydroxyphenyl)-2, 3-diphenyl-1, 3-propandione **34** in yellow plates (0.12 g), m.p. 165–7°. NMR: 6.58 (s, CHPh), 7.30–8.05 (m, Ar), 12.56 (s, OH).

A solution of the 1, 3-dione (2.0 g) in acetic anhydride (30 ml) and pyridine (8 drops) was worked-up as usual after 2 days, giving 1-(2-acetoxyphenyl)-2, 3-diphenyl-1, 3-propandione **35** in colourless plates (0.41 g), m.p. 110–3°. NMR: 2.15 (s, OAc), 6.54 (s, CHPh), 6.96–8.05 (m, Ar).

Bromine (0.11 g) in acetic acid (6 ml) was added slowly to a solution of the acetate (0.25 g) in acetic acid (4 ml). After 1 h, the usual work-up gave 1-(2-acetoxyphenyl)-2-bromo-2, 3-diphenyl-1, 3-propandione **36** as an oil (0.21 g). NMR: 2.11 (s, OAc), 7.00–8.05 (m, Ar).

Aqueous sodium hydroxide (0.2M; 3 ml) was added dropwise to a solution of the bromodiketone (0.05 g) in methanol (10 ml). After 1 h, the mixture was diluted with water and the precipitate was crystallized from benzene-hexane, giving 2, 3-diphenylchromone epoxide **29** in colourless needles (0.027 g), m.p. 128–130°.

3-Bromo-2-hydroxy-4, 6-dimethoxybenzil **41**

A solution of 2'-hydroxy-4',6'-dimethoxy-2-phenylacetophenone (7.0 g) in acetic anhydride (30 ml) was heated with sodium acetate (7.0 g) on a steam bath for 2 h, cooled, and poured into ice-water. The precipitate was crystallized, giving 2'-acetoxy-4', 6'-dimethoxy-2-phenylacetophenone **37** as colourless plates (5.48 g), m.p. 72–4°. NMR: 2.16 (s, OAc), 3.82 (s, 4'-OMe), 3.87 (s, 6'-OMe), 4.15 (s, CH_2), 6.30 (d, 3'-H; J2 Hz), 6.42 (d, 5'-H), 7.31 (s, Ph).

Bromine (2.13 g) in acetic acid (40 ml) was added to a solution of the acetate (4.2 g) in acetic acid (40 ml). After 1 h, the mixture was diluted with water and the precipitate crystallized from chloroform, giving 3'-bromo-2'-hydroxy-4', 6'-dimethoxy-2-phenylacetophenone **38** as colourless needles (3.25 g), m.p. 205–6° (lit.[19] m.p. 200–2°). NMR: 3.95 (s, 4'-OMe), 4.00 (s, 6'-OMe), 4.30 (s, CH_2), 6.08 (s, 5'-H), 7.35 (s, Ph), 14.55 (s, OH).

The bromoacetophenone (3.25 g) in acetic anhydride (12 ml) was heated with sodium acetate (3.25 g) on a steambath for 2 h, cooled, and poured into iced water. The precipitate was crystallized, giving 2'-acetoxy-3'-bromo-4', 6'-dimethoxy-2-phenylacetophenone **39** in colourless prisms (1.80 g), m.p 118–121°. NMR: 2.26 (s, OAc), 3.91 (s, 4'-OMe), 3.96 (s, 6'-OMe), 4.15 (s, CH_2), 6.46 (s, 5'-H), 7.32 (s, Ph).

Bromine (0.69 g) in acetic acid (30 ml) was added slowly to a solution of the acetate (1.70 g) in acetic acid (30 ml). After 1 h, the mixture was diluted with water and the precipitate was crystallized, giving 2'-acetoxy-2, 3'-dibromo-4', 6'-dimethoxy-2-phenylacetophenone **40** in colourless flakes (1.80 g), m.p. 126–9°. NMR: 2.29 (s, OAc), 3.88 (s, 4'-OMe), 3.95 (s, 6'-OMe), 6.20 (s, CHBr), 6.42 (s, 5'-H), 7.27–7.70 (m, Ar).

Aqueous sodium hydroxide (0.2 M; 11 ml) was added slowly to a solution of the dibromoacetophenone (0.50 g) in methanol (20 ml). After 1 h, and the usual work-up (without tlc), the residue was crystallized, giving 3-bromo-2-hydroxy-4, 6-dimethoxybenzil **41** as colourless prisms (0.20 g), m.p. 193–4°. NMR: 3.60 (s, 4-OMe), 4.02 (s, 6-OMe), 6.06 (s, 5-H), 7.34-8.00 (m, Ar).

3-Methoxymethyl-1, 2-methylchromone epoxide **43**

PTSA (trace) was added to a solution of 3-methoxymethyl-2-methyl-chromone epoxide[16] **43** in dry benzene (5 ml). After 2 days, the mixture was diluted with benzene and worked up as usual but using benzene in place of chloroform. The following were isolated in order of decreasing R_f values. 2-Methylchromonol **44** (0.04 g), m.p. 176–8° (lit[4] 178–180°); NMR: 2.52 (s, Me), 6.35 (s, OH), 7.20-7.85 (m, Ar), 8.35 (q, 5-H; J2 and 8 Hz). t - 3 - Hydroxy - r - 2 - methoxy - 3 - methoxymethyl - 2 - methyl - chromanone **46** an oil (0.25 g); NMR: 1.66 (s, 2-Me), 3.26 (s, 3-OMe), 3.34 (s, 2-OMe), 3.68 (d, 3-CH; J11 Hz), 3.84 (s, OH), 3.92 (d, 3-CH), 6.90–7.76 (m, Ar), 7.94 (q, 5-H; J2 and 8 Hz). t - 3 - Hydroxy - r - 2 - methoxymethoxy - 3 - methoxymethyl - 2 - methylchromanone **45** (0.025 g), m.p. 85–7°; NMR: 1.84 (s, 2-Me), 3.16 (s, 3-OMe), 3.23 (s, 2-OMe), 3.70 (d, 3-CH; J11 Hz), 3.92 (s, OH), 3.94 (d, 3-CH; J11 Hz), 4.64 (d, 2-OCH; J7 Hz), 4.92 (d, 2-OCH; J7 Hz), 6.90–7.75 (m, Ar), 7.94 (q, 5-H; J2 and 8 Hz).

PTSA (trace) was addet to a solution of the chromone epoxide **43** (0.10 g) in dry benzene (5 ml) containing ethanol (1 ml). After 12 h, the mixture was diluted with benzene and worked-up as usual but using benzene in place of chloroform. The following were isolated in order of decreasing R_f values: A diastereomer of 2-ethoxy-3-hydroxy-3-methoxymethyl-2-methylchromanone **47** as an oil (0.05 g); NMR: 1.16 (t, 2-OEt; J7 Hz), 1.59 (s, 2-Me), 3.41 (s, 3-OMe), 3.79 (q, 2-OEt; J7 Hz), 3.80 (d, 3-CH; J11 Hz), 4.00 (s, OH), 4.11 (d, 3-CH, J11 Hz), 6.90–7.80 (m, Ar), 7.93 (q, 5-H; J2 and 8 Hz). The second diastereomer of this chromanone **47** which crystallized from diethyl ether-hexane in colourless prisms (0.05 g), m.p. 86–8°; NMR: 0.90 (t, 2-OEt; J7 Hz), 1.65 (s, 2-Me), 3.31 (s, 3-OMe), 3.66 (d, 3-CH; J11 Hz), 3.68 (q, 2-OEt; J7 Hz), 3.80 (s, OH), 3.92 (d, 3-CH; J11 Hz), 6.91–7.80 (m, Ar), 7.96 (q, 5-H; J2 and 8 Hz). Both products (0.10 g) were individually dissolved in ethanol and PTSA (trace) was added. No reaction was observed (TLC) after 3 days.

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