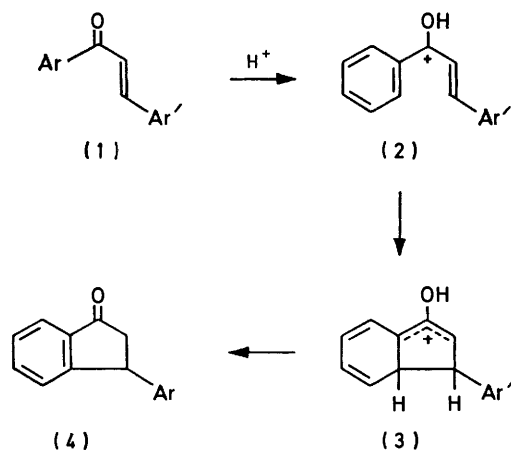


Electrocyclic Reactions of Protonated Chalcones: Synthesis of 3-Arylindan-1-ones

By Edward McDonald *† and Paul Smith, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW

A series of *ortho*-bromochalcones has been prepared and each has been heated and irradiated in strong acid. In most cases a four-electron electrocyclic reaction occurred preferentially to give 3-arylindan-1-ones in good yield. The acrylchalcone 4'-methoxy-3,3-bis-(4-methoxyphenyl)acrylophenone (26) failed to cyclise but underwent fragmentation yielding a diarylethylene (32).

PROTONATION of a *trans*-chalcone (1) should generate a linearly conjugated π -system (2) making possible a four-electron electrocyclic ring closure to the intermediate (3). The cyclisation might be induced thermally or photochemically with different stereochemical consequences¹ for the intermediate (3) but in both cases aromatisation would afford the indanone (4).



A protonated *cis*-chalcone (5) might also follow this pathway but two additional modes of cyclisation are now possible leading to the intermediate cations (6) and (7). If X and Y were a good leaving group and a proton (not necessarily respectively) then aromatisation of (7) would afford a dibenzo[*ac*]tropone ‡ (8), and we were particularly intrigued by the synthetic possibilities of this reaction. A close analogy is the well known photocyclisation³ of *cis*-stilbenes to phenanthrenes, the *cis*-stilbenes being generated *in situ* during irradiation of the readily available *trans*-isomers: *cis*- and *trans*-chalcones are similarly photoequilibrated.⁴ A series of *ortho*-bromochalcones was therefore prepared and their thermal and photochemical behaviour in strongly acidic media studied.

Synthesis of *ortho*-Bromochalcones.—The simple *trans*-chalcones (9)–(13) were prepared by base-catalysed condensation of the appropriately substituted benzaldehydes and acetophenones. The acetophenone (14) required for the chalcone (13) was obtained from the

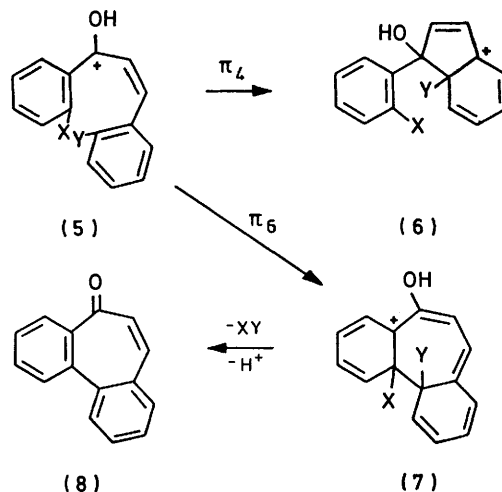
† Present address: I.C.I. Plant Protection Division, Jealott's Hill Research Station, Bracknell, Berkshire RG12 6EY.

‡ Dibenzo[*ac*]tropone has been prepared by a multi-step synthesis; see ref. 2.

nitrile (15)⁵ and methylmagnesium iodide *via* the imine (16), readily isolated and characterised as the hydrochloride salt. Hydrolysis of (16) required prolonged heating in aqueous oxalic acid, and its stability is attributed to the steric effect of the *ortho*-bromine substituents.

As an example of a chalcone with an obligatory *cis*-configuration, the aryl chalcone (17) was required. Bromination of 3,4-dimethoxyacetophenone under conditions similar to those used for the preparation of (18) gave the phenacyl bromide,⁶ rather than the required *ortho*-bromoacetophenone (19). The latter was therefore prepared from (18), by a Grignard reaction with methylmagnesium bromide followed by oxidation of the alcohol (20) with CrO₃-3,5-dimethylpyrazole.⁷ A direct condensation of (19) with 4,4-dimethoxybenzophenone was attempted but, as expected, none of the required chalcone (17) was obtained.

With such a benzophenone a highly reactive nucleophile was clearly required. The sodium and lithium

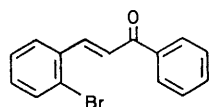


acetylides of (21)⁸ were therefore generated by reaction with NaH-THF and LiNPr₂-TNF, respectively: complete anion formation without side-reactions was indicated in each case by quenching an aliquot with D₂O and measuring the ¹H n.m.r. spectrum of the resultant deuterio-acetylene (22). Each acetylide was allowed to react with benzophenone, 4,4-dimethoxybenzophenone, and dichlorobis-(4-methoxyphenyl)methane⁹ under a wide range of conditions but no acetylenic alcohol was detected. Clearly the acetylides

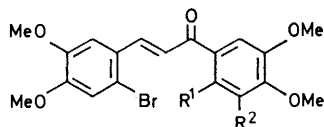
derived from (21) are less reactive than that from phenylacetylene.¹⁰

The chalcone (17) was finally prepared by 1,4-addition to (23) of the Grignard reagent from *p*-bromoanisole (in the presence of CuBr). The crude adduct (24) was oxidised by 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) to give the aryl chalcone (17) in excellent overall yield. The β -arylchalcone (26) was similarly prepared via (25).

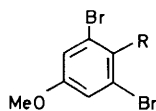
Thermal and Photochemical Reactions of the Protonated Chalcones.—Protonation of the chalcones (9)—(11) was easily monitored by u.v.-visible spectroscopy, the long-wavelength maxima shifting from 300 [for (9)], 370 [for (10)], and 360 [for (11)] (in MeOH) to 435, 520, and 535



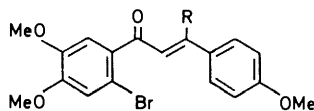
(9)



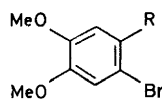
(10) $R^1 = R^2 = H$
 (11) $R^1 = H, R^2 = OMe$
 (12) $R^1 = Br, R^2 = H$



(14) $R = COCH_3$
 (15) $R = CN$
 (16) $R = C(Me) = NH$



(17) $R = 4$ -methoxyphenyl
 (23) $R = H$



(18) $R = CHO$
 (19) $R = COCH_3$
 (20) $R = CH(OH)Me$
 (21) $R = C \equiv CH$
 (22) $R = C \equiv CD$

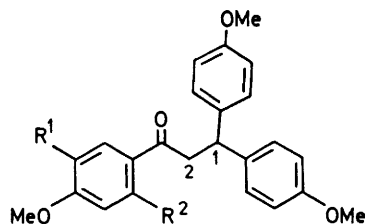
nm (in 98% H_2SO_4), respectively.* The three chalcones were recovered virtually unchanged when their solutions in sulphuric acid were poured into water after a short time.

When a 98% sulphuric acid solution of chalcone (9) was heated at 90 °C, the absorption at 435 nm slowly decreased in intensity and after 12 h a polar product was isolated in 40% yield. After treatment with diazomethane a less polar product, *m/e* 380 and 382 ($C_{16}H_{13}BrO_4S$) was obtained, showing that monosulphonation had occurred, and the indanone structure (27) is assigned to the cyclisation product on the basis of its spectra, particularly (a) an ABX pattern in the aliphatic region of the 1H n.m.r. spectra of (27) and ester (28) and (b) a second ABX pattern in the aromatic region of

* The pK_a values of several protonated chalcones have been estimated.¹¹

(28) (1,2,4-trisubstituted benzene) which was observed only in the presence of Eu(fod-d⁹) and after H-7 had disappeared to low-field with less shift reagent.

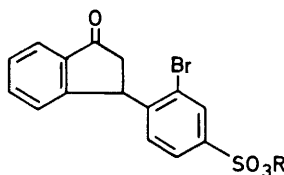
Under the same reaction conditions the tetramethoxychalcone (10) gave a complex mixture which was not further studied. However, (10) is more basic than (9) and unlike the latter is almost fully protonated even in trifluoroacetic acid (TFA). After refluxing for 24 h in



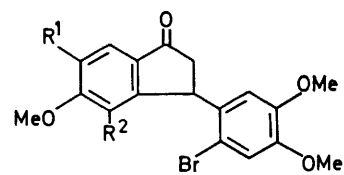
(24) $R^1 = OMe, R^2 = Br$
 (25) $R^1 = R^2 = H$
 (26) $R^1 = R^2 = H; 1,2$ -dehydro

this solvent the indanone (29) was isolated in 90% yield. The 1H n.m.r. spectrum provided the evidence for structure (29) rather than the alternative isomer (30) and the regiospecificity of the cyclisation is easily rationalised on steric grounds. The pentamethoxychalcone (11) similarly afforded the indanone (31) in quantitative yield after reflux for 6 h in trifluoroacetic acid, and (31) was also formed but less cleanly after 20 h in sulphuric acid at 20 °C.

Irradiation of the foregoing solutions of protonated chalcones (9)—(11) brought about a slower (possibly thermal) cyclisation to the same indanones and no new



(27) $R = H$
 (28) $R = Me$

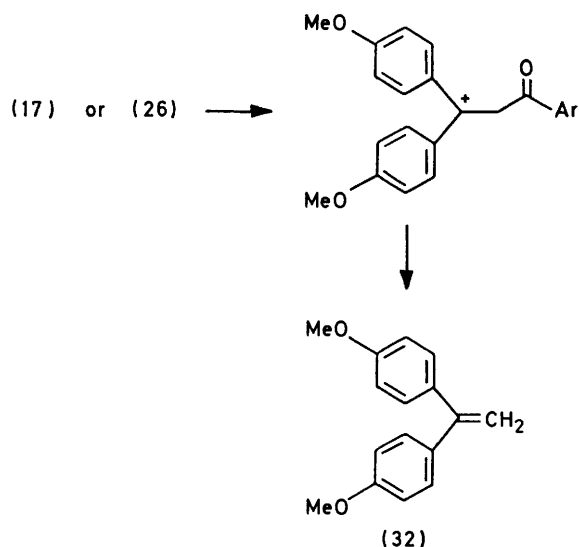


(29) $R^1 = OMe, R^2 = H$
 (30) $R^1 = H, R^2 = OMe$
 (31) $R^1 = R^2 = OMe$

products could be detected. The four-electron electrocyclic reaction is clearly the preferred reaction for simple *trans*-chalcones (9)—(11) and is probably faster than photochemical *trans-cis* isomerisation under the conditions we have studied.

In an effort to prevent the π_4 -electrocyclic process the chalcone (13), with bromine blocking-substituents, was prepared. Although the strategy was successful in preventing formation of indanone, no other reaction was observed under a variety of acidic conditions, even on irradiation. The β -arylchalcones (17) and (26) possess the structural elements of both a *trans*- and a *cis*-chalcone and so these molecules appeared to offer a

better opportunity for examining the relative rates of the pathways leading to intermediates of types (3), (6), and (7). In TFA the u.v. spectra of both compounds showed a strong absorption at *ca.* 525 nm which slowly disappeared on heating at 90 °C while a new peak appeared at *ca.* 495 nm. The *same* neutral product was isolated from both reactions and was shown to be the fragmentation product (32). A trace of the same product was also formed when solutions of (17) and (26) in TFA were irradiated, but no cyclisation products were detected. The formation of the diarylethylene (32) can be rationalised by the mechanism shown in which protonation of the β -arylchalcone on *carbon* rather than *oxygen* is followed by fragmentation to (32) and an acylium ion.



While this mechanism specifically requires a proton, a strong Lewis acid should be sufficient to generate the system (5) whose cyclisation we wished to study. Accordingly the chalcones (17) and (26) were heated under reflux and irradiated in ether with BF_3 and in nitromethane with AlCl_3 . As expected no fragmentation products were found but the chalcones were recovered unchanged. The activation energy for cyclisation to an indanone is evidently raised in these β -aryl chalcones by steric hindrance from the β -aryl substituent, but no six-electron electrocyclic reaction was observed.

Conclusion.—Protonated chalcones are converted cleanly and in high yield into the corresponding 3-arylindan-1-one. For oxygenated chalcones TFA is a sufficiently acidic medium for the reaction and the conditions are milder than those reported earlier for this type of conversion.* The reaction failed when either of the cyclisation termini was substituted and seems therefore to be sensitive to steric effects. However, even in these cases there was no sign of the alternative six-electron cyclisation to the intermediate (7), and we must

* Indanones have been prepared from chalcones both by AlCl_3 -catalysed^{12a} and polyphosphoric acid-catalysed cyclisation.^{12b}

conclude that the activation energy for this pathway is too high to permit an easy synthetic access to the dibenzotropone system (8).

EXPERIMENTAL

Except where stated otherwise, spectra were measured for solutions in chloroform (i.r.; Perkin-Elmer 257), 95% ethanol (u.v.; Unicam SP 800), and deuteriochloroform (n.m.r.; Varian HA-100). Unless stated otherwise chemical shifts are recorded as p.p.m. downfield from internal tetramethylsilane.

2,6-Dibromo-4-methoxyacetophenone (14).—Methylmagnesium iodide was prepared from magnesium turnings (1.1 g) and methyl iodide (4.3 ml) in dry ether (50 ml). A solution of 3,5-dibromo-4-cyanoanisoole (15) (3.2 g) in dry ether (25 ml) was added, and the mixture was heated under reflux for 15 h. The reaction mixture was poured onto ice and the ethereal layer extracted with 3*N*-HCl. The aqueous acidic extract was basified (3*N*-NaOH) and extracted with ether to give the crude imine (16) (2 g). An ethereal solution of the crude imine was treated with ethanolic HCl to give white crystals of 2,6-dibromo-4-methoxyacetophenone imine hydrochloride [cf. (16)] (1.2 g; 32%), m.p. 175° (from ethanol-ethyl acetate followed by sublimation) (Found: C, 31.7; H, 2.95; N, 4.1. $\text{C}_9\text{H}_{10}\text{Br}_2\text{ClNO}$ requires C, 31.25; H, 2.95; N, 3.95%), *m/e* 309, 307, and 305 (M^+), 284, 282, and 280 ($M^+ - \text{Me}$), and 228 and 226 ($M^+ - \text{Br}$), ν_{max} (Nujol) 2 600br, 1 590, 1 540, 850, and 750 cm^{-1} , λ_{max} 230, 280, and 287 nm, δ (in D_2O with Bu^tOH as reference) 2.86 (br, exchanges, $\ddot{\text{N}}\text{H}_2$), 3.86 (3 H, s, OMe), 4.70 (s, HOD peak), and 7.38 (2 H, s, ArH).

A solution of the foregoing imine hydrochloride [cf. (16)] (1.0 g) and oxalic acid (1.0 g) in water (25 ml) was heated under reflux for 14 h. Extraction with chloroform then gave the title acetophenone (14) (0.89 g; 95%), m.p. 50° (from ethanol) (Found: C, 34.95; H, 2.95. $\text{C}_9\text{H}_8\text{Br}_2\text{O}_2$ requires C, 35.1; H, 2.6%), *m/e* 310, 308, and 306 (M^+), 295, 293, and 291 ($M^+ - \text{Me}$), and 252, 250, and 248 ($M^+ - \text{Me} - \text{COCH}_3$), ν_{max} 1 710 and 1 590 cm^{-1} , λ_{max} 230, 280, and 289 nm, δ 2.35 (3 H, s, MeCO), 3.78 (3 H, s, OMe), and 7.04 (2 H, s, 2 ArH).

2',6'-Dibromo-3,4,4'-trimethoxychalcone (13).—3*N*-Aqueous sodium hydroxide (1 ml) was added to a hot solution of the acetophenone (31; 795 mg) and veratraldehyde (430 mg) in ethanol (20 ml), and the mixture was heated under reflux for 30 min. After evaporating to dryness the residue was extracted with dichloromethane. The solution was filtered, hexane added, and the yellow solution was heated (to remove dichloromethane) until it became cloudy. On cooling, fine yellow crystals of the chalcone (13) (850 mg; 70%) were deposited, m.p. 125–126° (from dichloromethane-hexane) (Found: C, 47.25; H, 3.85. $\text{C}_{18}\text{H}_{18}\text{Br}_2\text{O}_4$ requires C, 47.4; H, 3.55%), *m/e* 458, 456, and 454 (M^+), 443, 441, and 439 ($M^+ - \text{Me}$), 427, 425, and 423 ($M^+ - \text{OMe}$), and 377 ($M^+ - \text{Br}$), ν_{max} 1 640, 1 620, and 1 600 cm^{-1} , δ 3.83 and 3.89 (9 H, 3 OMe), and 6.7–7.3 (7 H, m, 5 ArH and 2 olefinic-H).

2-Bromo-4,5,3',4',5'-pentamethoxychalcone (11).—To a solution of 6-bromoveratraldehyde (18)¹³ (2.5 g) and 3,4,5-trimethoxyacetophenone (2.1 g) in boiling ethanol was added 2*N*-aqueous sodium hydroxide (3 ml). The solution was allowed to cool and a pale yellow precipitate was deposited of the chalcone (11) (3 g; 69%), m.p. 136–138° (from ethanol) (Found: C, 55.05; H, 4.65. $\text{C}_{20}\text{H}_{21}\text{BrO}_6$

requires C, 54.95; H, 4.8%), m/e 438 and 436 [M^+ (^{81}Br and ^{79}Br)], 407 and 405 (M^+ - OMe), and 358 (M^+ - Br), ν_{max} 1 660 and 1 590 cm^{-1} , λ_{max} (EtOH) 224, 255, 325, and 360, λ_{max} (TFA) 325, 275, and 500—550 (weak), λ_{max} (conc. H_2SO_4) 215, 370—430, and 525 nm, δ 3.92 (15 H, 5 OMe), 7.07, 7.19 (each 1 H, s, H-3 and -6), 7.23 (2 H, s, H-2' and H-6'), and 7.18 and 8.0 (each 1 H, d, J 15 Hz, *trans*-olefinic-H).

2-Bromo-4,5,3',4'-tetramethoxychalcone (10).—This chalcone was prepared from 6-bromoveratraldehyde (18)¹³ and 3,4-dimethoxyacetophenone in 98% yield by the procedure described above for (13), m.p. 166—167° (from acetone) (lit.¹⁴ 165—166°), m/e 408 and 406 (M^+), 377 and 375 (M^+ - OMe), and 327 (M^+ - Br), ν_{max} 1 653 and 1 598 cm^{-1} , δ 3.92, 3.95 (12 H, 4 OMe), 6.86 (1 H, d, J 8 Hz, H-5'), 7.02 (1 H, s, H-6), 7.14 (1 H, s, H-3), 7.55 (1 H, d, J 2 Hz, H-2'), 7.60 (1 H, dd, J 2 and 8 Hz, H-6'), and 7.24 and 7.98 (each 1 H, d, J 15 Hz, *trans*-olefinic-H).

2-Bromochalcone (9).—Prepared from acetophenone and 2-bromobenzaldehyde by base-catalysed condensation at room temperature, 2-bromochalcone (9) had m.p. 45—47° (from ethanol) (lit.¹⁵ 46—47°), m/e 288 and 286 (M^+), and 207 (M^+ - Br), ν_{max} (KBr disc) 1 665 and 1 610 cm^{-1} , δ 7.04—8.14 (complex m).

6-Bromo-3,4-dimethoxy- α -methylbenzyl Alcohol (20).—Methylmagnesium iodide was prepared by slowly adding a solution of methyl iodide (21 g) in dry ether (100 ml) to magnesium turnings (3.6 g) in ether (20 ml) so as to maintain a steady reflux. After 30 min, dry tetrahydrofuran (THF) (100 ml) was added and most of the ether was distilled off.

After cooling to 20 °C a solution of 6-bromoveratraldehyde¹³ (18) (7.5 g) in dry THF (100 ml) was added and the reaction mixture was stirred for 30 min, then poured onto ice. Acetic acid was added until the solution became clear and extraction with ethyl acetate gave the crude alcohol (20) (8 g; 100%) which was used directly for the next step, m/e 262 and 260 (M^+), 247 and 245 (M^+ - Me), 244 and 242 (M^+ - H_2O), and 148 (M^+ - H_2O - Me - Br), ν_{max} 3 580, 3 460, and 1 600 cm^{-1} , λ_{max} 215, 233, and 285 nm, δ 1.38 (3 H, d) and 5.10 (1 H, q), (each J 6 Hz, CH_3CH), 2.62 (1 H, br s, OH), 3.80 (6 H, 2 OMe), and 6.88 and 7.04 (each 1 H, s, 2 ArH).

2-Bromo-4,5-dimethoxyacetophenone (19).—3,5-Dimethylpyrazole (19.2 g) was added to a solution of chromium trioxide (20 g) in dichloromethane (200 ml). After stirring for 15 min a solution of the foregoing crude alcohol (20) (26.1 g) in dichloromethane (50 ml) was added over 5 min. The brown solution was kept at 20 °C for 24 h and the solvent was then removed (Rotovap). The residue was triturated with 3:1 v/v ether-dichloromethane, then filtered off. Evaporation of the filtrate left a brown oil which was chromatographed on silica (Fisons; 100—200 mesh; 200 g) eluting with ether. The acetophenone (19) was obtained as a pale yellow solid (16 g; 80%) by evaporation of the eluate; m.p. 74—76° (from ethanol after repeated recrystallisation) (lit.⁸ 106°) (Found: C, 46.25; H, 4.25. Calc. for $\text{C}_{10}\text{H}_{11}\text{BrO}_3$: C, 46.35; H, 4.3%), m/e 260 and 258 (M^+), and 245 and 243 (M^+ - Me), ν_{max} 1 680 and 1 600 cm^{-1} , λ_{max} 232, 273, 292, and 305sh nm, δ 2.64 (3 H, s, MeCO), 3.86 and 3.88 (each 3 H, s, 2 OMe), and 7.02 and 7.12 (each 1 H, s, 2 ArH).

2,2'-Dibromo-4,4',5,5'-tetramethoxychalcone (12).—A solution of 6-bromoveratraldehyde (1.42 g) and the acetophenone (19) (1.50 g) in ethanol (25 ml) was heated on a

steam-bath for 30 min with 3*N*-aqueous NaOH (1.9 ml). On cooling, a yellow precipitate of the *chalcone* (12) was produced (2.7 g; 95%), m.p. 170—171° (from dichloromethane-hexane) (Found: C, 46.0; H, 3.75. $\text{C}_{17}\text{H}_{16}\text{Br}_2\text{O}_5$ requires C, 46.95; H, 3.75%), m/e 488, 486, and 484 (M^+), 407 and 405 (M^+ - Br), and 392 and 390 (M^+ - Br - Me), ν_{max} 1 600 and 1 650, λ_{max} 250, 315sh, and 357 nm, δ 3.86 (12 H, 4 OMe), 6.96 and 7.80 (each 1 H, d, J 18 Hz, $\text{ArCH}=\text{CHCO}$), and 7.00, 7.02, 7.04, and 7.14 (each 1 H, s, 4 ArH).

2'-Bromo-4,4',5'-trimethoxychalcone (23).—A solution of the acetophenone (19) (10 g) and anisaldehyde (4.8 ml) in ethanol (40 ml) was heated on a steam-bath for 30 min with 3*N*-aqueous sodium hydroxide (12.8 ml). The solution was cooled and the yellow crystalline product collected and recrystallised from dichloromethane-hexane to give the *chalcone* (23) (13 g; 90%), m.p. 179—180° (Found: C, 57.15; H, 4.45. $\text{C}_{18}\text{H}_{17}\text{BrO}_4$ requires C, 57.3; H, 4.55%), m/e 378 and 376 (M^+), 363 and 361 (M^+ - Me), and 297 (M^+ - Br), ν_{max} 1 650 and 1 600 cm^{-1} , δ 3.80, 3.84, and 3.88 (each 3 H, s, 3 OMe), 6.98 and 7.04 (each 1 H, s, 2 ArH), 6.88 and 7.50 (each 2 H, d, J 8 Hz, 4 ArH), and 7.02 and 7.47 (each 1 H, d, J 14 Hz, *trans*-olefinic-H).

2'-Bromo-4',5'-dimethoxy-3,3-bis-(4-methoxyphenyl)propio-phenone (24).—4-Methoxyphenylmagnesium bromide was prepared by adding a solution of 4-bromoanisole (13 ml) in dry ether (125 ml) to magnesium turnings (2.4 g) stirred under dry ether (20 ml). The rate of addition was adjusted to maintain a steady reflux and when complete, the mixture was heated under reflux for a further 30 min. Dry THF was then added to give a homogeneous solution of the Grignard reagent.

The solution was cooled in an ice-bath and a solution of the foregoing *chalcone* (23) (8 g) in dry THF (150 ml) was added dropwise together with cuprous bromide (in three portions; total 1.3 g). After stirring for 1 h, the reaction mixture was added to a rapidly stirred solution of ammonium chloride (100 g) in water (500 ml) and the solution was extracted with ether. The ether extract on evaporation gave a yellow oil (*ca.* 18 g) which was chromatographed on neutral alumina (Woelm, grade III; 300 g). Elution with 9:1 v/v cyclohexane-ether gave the by-product 4,4'-dimethoxybiphenyl, m.p. 175—177° (from benzene) (lit.¹⁸ 176—178°), m/e 214 (M^+), 199 (M^+ - Me), and 171 (M^+ - Me - CO) with metastable peaks at 185, 147 indicating the fragmentations $214 \rightarrow 199 \rightarrow 171$, ν_{max} 1 605 cm^{-1} , λ_{max} 212 and 257 nm, δ 3.80 (6 H, s, 2 OMe), 6.92 and 7.45 (each 4 H, d, J 8 Hz, 8 ArH).

Further elution with 4:1 v/v cyclohexane-ether afforded the *propio-phenone* (24) (5 g; 50%), m.p. 103—105° (from dichloromethane-hexane) (Found: C, 62.0; H, 5.3. $\text{C}_{25}\text{H}_{25}\text{BrO}_5$ requires C, 61.9; H, 5.19%), m/e 486 and 484 (M^+), 405 (M^+ - Br), 245 and 243 (ArCO), and 227 (Ar_2CH), ν_{max} 1 680 and 1 600 cm^{-1} , λ_{max} 236, 275, and 300 nm, δ 3.66 (2 H, d) and 4.58 (1 H, t) (each J 7 Hz, $\text{COCH}_2\text{-CHAr}_2$), 3.67, 3.69, 3.70, and 3.85 (each 3 H, s, 4 OMe), 6.46 and 6.96 (each 1 H, s, 2 ArH), and 6.76 and 7.10 (each 4 H, d, J 8 Hz, 8 ArH).

4'-Methoxy-3,3-bis-(4-methoxyphenyl)propio-phenone (25).—4-Methoxyphenylmagnesium bromide was prepared as above and on the same scale and a solution of 4,4'-dimethoxychalcone (8 g) in dry THF (100 ml) was added together with cuprous bromide (1.3 g). The reaction was completed as before except that chromatography was

avoided by using the crude product (contaminated with 4,4'-dimethoxybiphenyl) (*ca.* 19 g) directly for the next step. A small sample (150 mg) was, however, purified by preparative t.l.c. on alumina, eluting with 1:1 dichloromethane-cyclohexane, to afford the propiophenone (25) (76 mg), m.p. 82–84° (from dichloromethane-hexane) (lit.,¹⁷ 83–84°), *m/e* 376 (M^+), 227 (Ar_2CH^+), and 135 (ArCO^+), ν_{max} 1 670 and 1 600 cm^{-1} , λ_{max} 225 and 275 nm, δ 3.59 (2 H, d) and 4.71 (1 H, t) (each J 6 Hz, $\text{CO}-\text{CH}_2\text{CHAr}_2$), 3.71 (6 H, s) and 3.82 (3 H, s) (3 OMe), 6.77 and 7.13 (each 4 H, d, J 8 Hz, 8 ArH), and 6.88 and 7.88 (each 2 H, d, J 8 Hz, 4 ArH).

4'-Methoxy-3,3-bis-(4-methoxyphenyl)acrylophenone (26).—A solution of the foregoing crude propiophenone (25) (7 g) in benzene (100 ml) was heated under reflux for 2 h with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) (3 g). After cooling, the reaction mixture was filtered and the filtrate evaporated to dryness. The residue was absorbed onto silica and introduced to the top of a silica column packed in hexane. Elution with benzene afforded the by-product 4,4'-dimethoxybiphenyl, and the solvent polarity was gradually increased, the oily acrylophenone (26) being eluted by dichloromethane, *m/e* 374 (M^+), 373 ($M^+ - \text{H}$), 359 ($M^+ - \text{CH}_3$, m^* at 344), 267 ($M^+ - \text{C}_6\text{H}_4 - \text{OMe}$), and 135 (ArCO^+), ν_{max} 1 650 and 1 600 cm^{-1} , δ 3.76 (3 H, s) and 3.81 (6 H, s) (3 OMe), 6.70–7.40 (9 H, m, 8 ArH and olefinic-H), and 6.83 and 7.90 (each 2 H, d, J 8 Hz, 4 ArH).

2'-Bromo-4',5'-dimethoxy-3,3-bis-(4-methoxyphenyl)acrylophenone (17).—A solution of the propiophenone (24) (4.6 g) in benzene (50 ml) was heated under reflux for 3 h with DDQ (2.3 g). After cooling, the reaction mixture was filtered and the filtrate evaporated to dryness. The residue was chromatographed on neutral alumina (Woelm, grade III; 60 g), eluting with 1:1 *v/v* cyclohexane-dichloromethane, to give the bright yellow acrylophenone (17) (4.4 g; 95%), m.p. 105–106° (from dichloromethane-cyclohexane) (Found: C, 62.35; H, 4.85. $\text{C}_{25}\text{H}_{23}\text{BrO}_5$ requires C, 62.1; H, 4.8%), *m/e* 484 and 482 (M^+), 483 and 481 ($M^+ - \text{H}$), 469 and 467 ($M^+ - \text{CH}_3$), and 403 ($M^+ - \text{Br}$), ν_{max} 1 640 and 1 600 cm^{-1} , δ 3.76 and 3.80 (12 H, 4 OMe), and 6.6–7.4 (11 H, m, 10 ArH and olefinic-H).

Acid-catalysed Cyclisation-Sulphonation of 2-Bromo-chalcone (9).—A bright orange solution of 2-bromochalcone (9) (300 mg) in 98% sulphuric acid (20 ml) was heated at 90 °C for 12 h. During this time the u.v. absorption at λ_{max} 430 nm disappeared and new maxima appeared at λ_{max} 285 and 345 nm. The solution was cooled and poured onto ice. Extraction with ethyl acetate gave the indanone sulphonic acid (27) as a colourless oil (200 mg), ν_{max} (Nujol) 3 450br and 1 705 cm^{-1} , λ_{max} 220, 235, and 290 nm, δ ($\text{CDCl}_3-\text{CD}_3\text{OD}$) 2.60 (1 H, dd, J 4 and 19 Hz, H_A), 3.34 (1 H, dd, J 8 and 19 Hz, H_B), 5.16 (1 H, dd, J 4 and 8 Hz, H_X) ($-\text{CO}-\text{CH}_A\text{H}_B-\text{CH}_X\text{Ar}-$), 4.67 (br s, exchanges, OH), and 7.32–7.82 (7 H, m, 7 ArH). The acid was suspended in a little methanol and treated with ethereal diazomethane until the distinctive yellow colour persisted. Evaporation of the solvent gave the oily sulphonate ester (28), *m/e* 382 and 380 (M^+), δ 2.56, 3.37, and 5.14 (each 1 H, dd, ABX system, J_{AB} 18.5, J_{AX} 4, J_{BX} 8 Hz), 3.70 (3 H, s, OMe), and 7.26–7.88 (7 H, m, ArH). Addition of $\text{Eu}(\text{fod})_3$ portionwise eventually simplified the aromatic signals which now appeared at δ 8.08 (d, J 8 Hz), 8.23 (dd, J 2 and 8 Hz), and 9.00 (d, J 2 Hz) (proves the presence of a 1,2,4-trisubstituted benzene ring, the signals being assigned here to

H-6', -5', and -3', respectively), 8.44 (3 H, br s, H-4, -5, and -6), and 11.4 (1 H, br signal now, H-7).

3-(2-Bromo-4,5-dimethoxyphenyl)-5,6-dimethoxyindan-1-one (29).—A red solution of the chalcone (10) (100 mg) in trifluoroacetic acid (20 ml) was heated under reflux for 24 h. The absorption at λ_{max} 520 nm disappeared and was replaced by maxima at 280 and 320 nm. The solution was poured onto ice and extracted with ethyl acetate. After evaporation of the solvent the residue was triturated with ethanol to give the indanone (29) as a pale yellow solid (70 mg), m.p. 194–196° (from ethanol) (Found: M^+ , 408.0403 and 406.0410. $\text{C}_{19}\text{H}_{19}\text{BrO}_5$ requires M^+ , 408.0395 and 406.0414), *m/e* 408 and 406 (M^+), 377 and 375 ($M^+ - \text{OMe}$), and 327 ($M^+ - \text{Br}$), ν_{max} 1 690 and 1 595 cm^{-1} , λ_{max} 235, 270, 295, and 312 nm, δ 2.51, 3.28, and 4.95 (each 1 H, dd, ABX system, J_{AB} 18, J_{AX} 2, and J_{BX} 8 Hz, $-\text{CO}-\text{CH}_A\text{H}_B\text{CH}_X\text{Ar}-$), 3.64, 3.86, and 3.93 (12 H, 4 OMe), and 6.31, 6.72, 7.06, and 7.22 (each 1 H, s, 4 ArH).

3-(2-Bromo-4,5-dimethoxyphenyl)-4,5,6-trimethoxyindan-1-one (31).—A red solution of the chalcone (11) (100 mg) in trifluoroacetic acid (20 ml) (λ_{max} 500–550 nm) was heated under reflux for 6 h, by which time the solution was pale yellow (λ_{max} 345 nm). The reaction mixture was worked up as above to give the indanone (31) as a colourless oil (80 mg) which crystallised when triturated under cyclohexane, m.p. 121–122° (from dichloromethane-hexane) (Found: C, 54.8; H, 4.8. $\text{C}_{20}\text{H}_{21}\text{BrO}_6$ requires C, 54.95; H, 4.85%), *m/e* 438 and 436 (M^+), 407 and 405 ($M^+ - \text{OMe}$), and 358 ($M^+ - \text{Br}$), ν_{max} 1 705 and 1 605 cm^{-1} , λ_{max} 213, 225, 276, and 305–315 nm, δ 2.48, 3.22, and 4.98 (each 1 H, dd, ABX system, J_{AB} 18, J_{AX} 2, and J_{BX} 8 Hz, $\text{CO}-\text{CH}_A\text{H}_B\text{CH}_X\text{Ar}-$), 3.52, 3.59, 3.83, and 3.88 (15 H total, 5 OMe), and 6.18, 7.02, and 7.06 (each 1 H, s, 3 ArH).

1,1-Bis-(*p*-methoxyphenyl)ethylene (32) from Fragmentation of (26).—A solution of the acrylophenone (26) (100 mg) in TFA (20 ml) was heated under reflux for 24 h. The deep red solution initially had λ_{max} 520 nm and this peak almost disappeared, a new peak appearing at λ_{max} 495 nm. The reaction mixture was cooled, poured onto ice, basified with sodium carbonate, and extracted with ethyl acetate. The organic phase was evaporated to dryness and the residue fractionated by preparative t.l.c. to give 1,1-bis-(*p*-methoxyphenyl)ethylene (35 mg; 55%), m.p. 141–142° (from dichloromethane-hexane) (lit.,¹⁸ 142°), *m/e* 240 (M^+), 225 ($M^+ - \text{CH}_3$), ν_{max} 1 600 cm^{-1} , λ_{max} (EtOH) 230 and 255–270 nm, λ_{max} (TFA) 335 and 495 nm, δ 3.78 (6 H, s, 2 OMe), 5.27 (2 H, s, 2 olefinic H), and 6.86 and 7.26 (each 4 H, d, J 8 Hz, 8 ArH).

Photochemical Studies on the Chalcones.—Each chalcone was dissolved in 98% sulphuric acid, or trifluoroacetic acid, and was irradiated using a Hanovia 125 watt medium pressure mercury lamp fitted with a quartz cold finger. The heat generated by the lamp was always sufficient to cause a rise in temperature of the solutions, and it is possible that the small yields of indanone which were formed, arose from thermal rather than photochemical cyclisation. However, no other products were observed after 1–2 days and the experiments were terminated.

We thank the S.R.C. for financial support.

[9/737 Received, 14th May, 1979]

REFERENCES

- 1 R. B. Woodward and R. Hoffmann in 'The Conservation of Orbital Symmetry,' Verlag Chemie, 1970, p. 58.

- ² G. Neville, H. Strauss, and E. Heilbronner, *Helv. Chim. Acta*, 1960, 1221 and references therein.
- ³ For a recent review see E. V. Blackburn and C. J. Timmons, *Quart. Rev.*, 1969, **23**, 482.
- ⁴ W. B. Black and R. E. Lutz, *J. Amer. Chem. Soc.*, 1955, **77**, 5134.
- ⁵ E. Burer and M. Nedelkova, *Casopis Ceskoslov Lekarnicka*, 1929, **9**, 23 (*Chem. Abs.*, 1929, **23**, 3675).
- ⁶ C. Mannich and F. L. Hahn, *Chem. Ber.*, 1911, **44**, 1549.
- ⁷ E. J. Corey and G. W. J. Fleet, *Tetrahedron Letters*, 1973, 4499.
- ⁸ K. W. Bentley, S. F. Dyke, and A. R. Marshall, *J. Chem. Soc.*, 1963, 3914.
- ⁹ H. Staudinger, K. Clar, and E. Czako, *Chem. Ber.*, 1911, **44**, 1645.
- ¹⁰ cf. J. V. Nef, *Annalen*, 1899, **308**, 282. We have repeated this reaction without difficulty.
- ¹¹ D. S. Noyce and M. J. Jorgenson, *J. Amer. Chem. Soc.*, 1962, **84**, 4312.
- ¹² (a) D. B. Bruce, A. J. S. Sorrie, and R. H. Thomson, *J. Chem. Soc.*, 1953, 2403; C. F. Koelsch, *J. Org. Chem.*, 1961, **26**, 2590; (b) J. M. Allen, K. M. Johnston, J. F. Jones, and R. G. Schotter, *Tetrahedron*, 1977, **33**, 2083.
- ¹³ R. Pschorr, *Annalen*, 1912, **391**, 32.
- ¹⁴ A. S. Bailey and R. Robinson, *J. Chem. Soc.*, 1950, 1375.
- ¹⁵ N. L. Silver and D. W. Boykin, *J. Org. Chem.*, 1970, **35**, 759.
- ¹⁶ F. Ullman and O. Lowenthal, *Annalen*, 1904, **332**, 67.
- ¹⁷ A. H. Stuart and R. C. Tallman, *J. Amer. Chem. Soc.*, 1943 **65**, 1579.
- ¹⁸ L. Gatterman, *Chem. Ber.*, 1889, **22**, 1132.