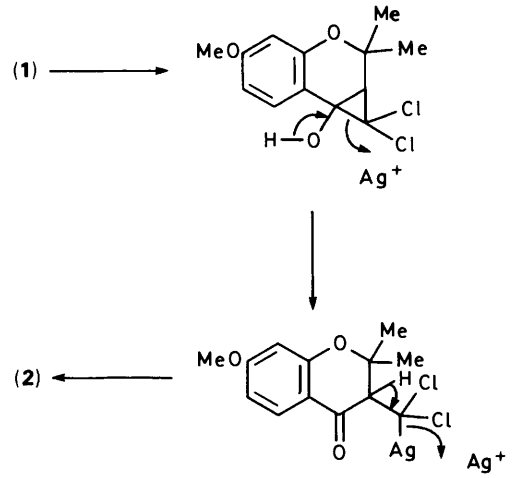
# Studies of Chromenes. Part 8.[1] Addition *versus* Rearrangement in Silver Ion-assisted Solvolyses of Trihalogenocyclopropa[*c*]chromenes

**Philip E. Brown,* William Clegg, Qamrul Islam, and John E. Steele**
*Department of Chemistry, The University, Newcastle upon Tyne, NE1 7RU*

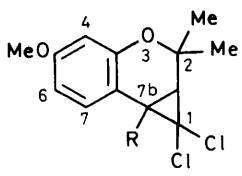
Silver ion-assisted solvolysis of the trichlorocyclopropa[*c*]chromene (**1**) at 80 °C proceeds by addition to give the 3-dichloromethylenechroman-4-one (**2**). At higher temperatures solvolysis involves cyclopropyl-allyl rearrangement and yields derivatives of the 4-dichloromethylenechroman-3-ol. The 7b-bromo-1,1-dichlorocyclopropa[*c*]chromene (**9**) reacts by rearrangement even at 80 °C.

We have previously reported[2] that the trichlorocyclopropachromene (**1**) affords the 3-dichloromethylenechroman-4-one (**2**) on silver ion-assisted solvolysis in moist acetonitrile. The structure of the product, whose yield has been raised to over 90%, was secured by *X*-ray crystallography (Figure 1).

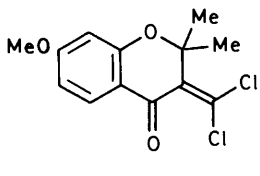
Silver ion-assisted ring-opening of halogenocyclopropanes usually proceeds *via* cyclopropyl-allyl rearrangement; loss of the halide and rearrangement are concerted so that a cyclopropyl cation is not normally an intermediate.[3] Formation of the above product (**2**) clearly does not involve such a rearrangement since loss of a gem chloride would lead to a benzoxepine whilst loss of the benzylic chloride would lead either to a 4-dichloromethylene derivative or, however unlikely, to a chromene-3-carboxylic acid. We suggested that the mechanism of this reaction might involve hydrolysis of the 4-chloride to a cyclopropanol (**3**) which could then undergo typical ring-opening,[4] subsequent oxidative elimination of silver providing the product (**2**) (Scheme 1). It was also pointed out, however, that the reaction could be regarded as an addition across the 1–7b bond.



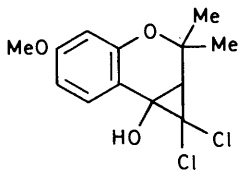

**Scheme 1.** Formation of the ketone (**2**) *via* a cyclopropyl intermediate




(**1**) R = Cl
(**9**) R = Br




(**2**)

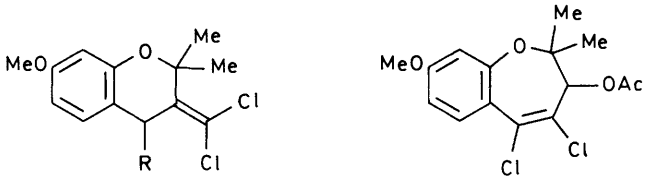



(**3**)

Although cyclopropyl halides are generally highly unreactive towards substitution the intermediacy of the cyclopropanol (**3**) was considered since several solvolyses in which the cyclopropane ring remains intact are known.[5–7] Such reactions tend to occur when the corresponding cyclopropyl cations are particularly stable[8] or when the disrotation required for concerted rearrangement is sterically inhibited, as occurs with loss of the more accessible *exo* halide of cyclohexane-fused cyclopropyl gem-dihalides.[9] In the cyclopropachromene (**1**) both electronic and steric factors would lead to loss of the 7b-halide whilst electronic factors make formation of a cyclopropyl cation, and thence a cyclopropanol intermediate on solvolysis, a reasonable possibility.

Attempts to trap the proposed intermediate cyclopropyl cation by solvolysis with silver acetate in acetic acid at 80 °C afforded the same product (**2**) together with a small quantity of a dichloroacetoxy species. The yield of the latter was raised to over 80% by increasing the reaction temperature to the boiling point. The new material was not, however, a cyclopropyl derivative since its $^1$H n.mr. spectrum did not possess a 1a-H signal at δ 2—3; instead a signal at δ 5.99 was assigned to an allylic C*H*OAc. Of the alternative ring-opened structures (**4**), (**6**), and (**7**) the 4-acetate (**4**) is mechanistically unlikely and δ 5.99 low for a proton flanked by acetoxy, aryl, and vinyl groups; moreover, this structure could be eliminated since nuclear Overhauser enhancements of 10 to 12% were observed for the proton at δ 5.99 on irradiation of each of the gem-dimethyl groups. Additionally the acetate could be converted into an alcohol different from that, (**5**), obtained by reduction of the chroman-4-one (**2**). Although the possible structure (**6**) requires the less likely loss of a gem-chloride, rigorous distinction between this and the alternative structure (**7**) was not possible spectroscopically. The alcohol resisted oxidation so that u.v. spectroscopy could not be used to distinguish between the extended and cross-conjugated ketones related to structures (**6**) and (**7**).

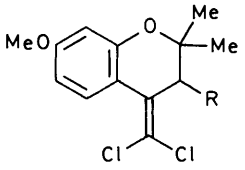
Despite both the acetate and its parent alcohol being crystalline solids, crystals suitable for *X*-ray crystallography could not be obtained. However, by replacing the silver acetate with silver nitrate, a nitrate ester was formed which gave satisfactory crystals; subsequent crystallography confirmed structure (**8**), a



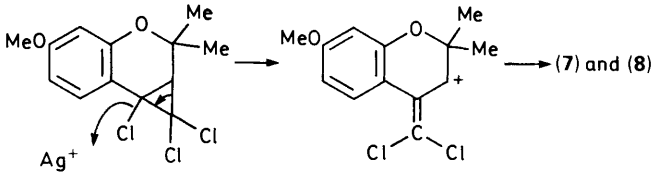
(4) R = OAc
(5) R = OH



(6)



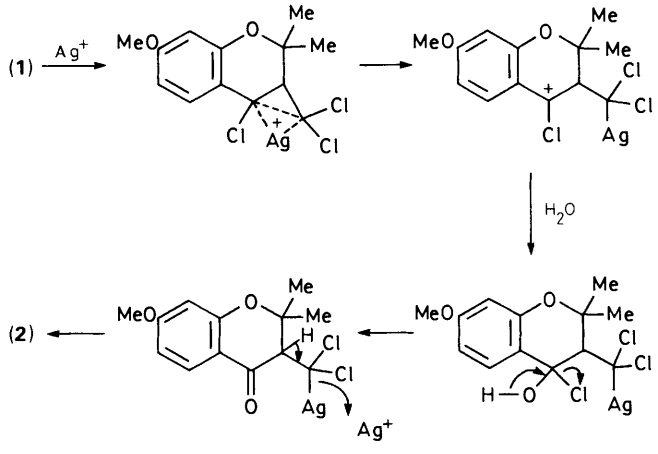
(7) R = OAc
(8) R = $ONO_2$



Scheme 2. Formation of the esters (7) and (8) *via* cyclopropyl-allyl rearrangement

product of cyclopropyl–allyl rearrangement (Figure 2). We were unable to convert the nitrate into its parent alcohol and nor could we form a nitrate from the alcohol derived from the aceate. Nevertheless, it seems likely that both the nitrate and acetate are derived from the same alcohol. Confirmation of this was obtained by solvolysis of the 7b-bromodichlorocyclopropachromene (**9**) in which the more nucleofugic 7b-bromide was expected to make addition relatively less favoured. When this substrate was subjected to assisted solvolysis in acetic acid the dichloroacetate was obtained in over 90% yield even at 80 °C, showing that removal of a gem chloride is not involved and that this product cannot have the structure (**6**) and must therefore be the chromanoid 3-acetate (**7**).

The results give no evidence of cyclopropanol formation and show that at higher temperatures the trichlorocyclopropachromene (**1**) is solvolysed by typical rearrangement involving loss of the benzylic chloride (Scheme 2). At lower temperatures



Scheme 3. Formation of the ketone (**2**) *via* addition of silver ion

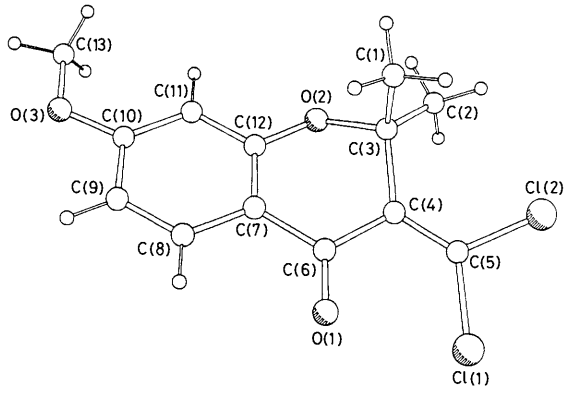


Figure 1. *X*-Ray crystal structure and crystallographic numbering scheme for compound (**2**)

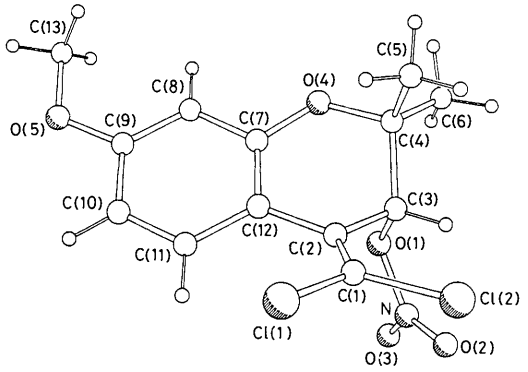
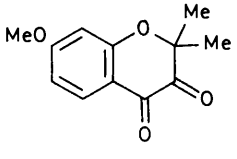


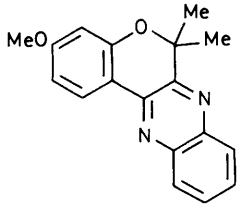
Figure 2. *X*-Ray structure and crystallographic numbering scheme for compound (**8**)

an alternative reaction, consistent with direct addition of the silver ion to either an edge or a corner, occurs. This is illustrated for edge addition to the 1,7b bond in Scheme 3. Precedents for the cleavage of cyclopropanes assisted by silver and other metal ions[10,11] are well known and, although halogencyclopropanes are more resistant to acid cleavage, in the present case stabilisation of positive charge at C-7b and of negative charge at C-1 could make this a lower-energy pathway than either concerted or non-concerted removal of the 7b-chloride. Thus, by choice of the original 4-halogenochromene from which the cyclopropanes are prepared, products from each solvolytic mode can be obtained with high yield and selectivity.

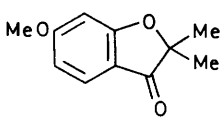
Silver ion-assisted methanolyses of two dibromocyclopropanes have been shown to involve both termolecular (second order in silver ion) and bimolecular (first order in silver ion)



(10)



(11)



(12)

processes, the rate constants for the former being about 10 times those of the latter.[12] The relative importance of the two solvolytic modes observed in the present work is therefore probably highly sensitive to the silver ion concentration as well as being dependent on the temperature and the leaving group.

In order consistently to achieve these results careful attention to experimental detail is required, otherwise mixtures of some of the above compounds and a number of by-products are formed. One such by-product was shown to be the chroman-3,4-dione (**10**) by formation of the quinoxaline (**11**). The dione was eluted from silica gel as a methanolic hemiacetal recognisable by the additional methoxy signal at δ 2.97 and the two distinct gem dimethyl signals. The methanol adduct, presumed to involve the 4-carbonyl group on steric grounds, was slowly decomposed on azeotropic distillation with toluene. The 3,4-dione could also be identified in the crude reaction product by mass spectrometry; the parent ion was readily seen but the presence of a carbonyl group adjacent to C-2 inhibits formation of an ($M$ − 15) fragment normally characteristic of 2,2-dimethylchromanoids. Mass spectrometry also indicated the formation of a compound consistent with structure (**12**); again no ($M$ − 15) peak corresponding to this compound was observed. These by-products may be rationalised as being derived either *via* the rearrangement or the addition solvolytic mode, conversion of the dichloromethylene moieties into carbonyl groups possibly taking place by retrograde aldol reactions following hydration.

## Experimental

M.p.s (Kofler hot-stage) are uncorrected. I.r. spectra were recorded on a Nicolet 20 SXB FT instrument and u.v. spectra determined with a Perkin-Elmer Model 137 instrument. $^1$H (60 MHz) N.m.r. spectra were obtained on a Perkin-Elmer R24 machine with tetramethylsilane as internal standard; the $^{13}$C n.m.r. spectrum was obtained on a Brüker WP-200 spectrometer (working at 50 MHz). Mass spectra were obtained on either an AEI MS9 or a Kratos MS80 instrument. Elemental analyses were performed with a Carlo Erba Model 1106 CHN machine. Homogeneity of non-crystalline compounds was established by t.l.c. in at least three solvents of differing polarities. Ether refers to diethyl ether and light petroleum to that fraction with b.p. 40—690 °C.

1,1,7b-*Trichloro*-1a,7b-*dihydro*-5-*methoxy*-2,2-*dimethylcyclopropa*[c]*chromene* (**1**).—(a) *Phase-transfer conditions.* A solution of sodium hydroxide (23 g, 0.575 mol) in water (25 ml) was added over 30 min to a vigorously stirred solution of 4-chloro-7-methoxy-2,2-dimethylchromene[13] (2.482 g, 11.05 mmol) in chloroform (38 ml) containing benzyltriethylammonium chloride (125 mg) at room temperature. Stirring was continued until all starting material had reacted (t.l.c., *ca.* 3 h) and the organic and aqueous phases were then separated. The aqueous layer was extracted with chloroform (3 × 20 ml) and the combined organic phases were dried ($MgSO_4$). Removal of the solvent left a residue which was passed down a short column of silica gel (dichloromethane – light petroleum as eluant). The first material eluted was the title trichlorocyclopropachromene (**1**) (5.57 g, 81%) obtained as colourless *prisms*, m.p. 84 °C (from light petroleum); $\nu_{max.}$(KBr) 1 620, 1 580, and 1 503 cm$^{-1}$; δ($CDCl_3$) 1.37 and 1.67 (each 3 H, s), 2.22 (1 H, s, 1a-H), 3.76 (3 H, s), 6.25 (1 H, d, $J$ 2 Hz), 6.54 (1 H, dd, $J$ 9 and 2 Hz), and 7.60 (1 H, d, $J$ 9 Hz) (Found: C, 50.75; H, 4.15%; $M^+$, 306.0012. $C_{15}H_{13}Cl_3O_2$ requires C, 50.76; H, 4.26% $M$, 305.9981).

(b) *From sodium trichloroacetate.* Dry sodium trichloroacetate (21.6 g, 117 mmol) was added over 2 days to a vigorously stirred boiling solution of 4-chloro-7-methoxy-2,2-dimethylchromene (4.0 g, 17.8 mmol) in dry tetrachloroethylene (125 ml) and dry 1,2-dimethoxyethane (50 ml). When all starting material had reacted (t.l.c.) the reaction mixture was filtered and concentrated to give a brown oil. This was decolourised by passage down a short column of silica gel (dichloromethane–light petroleum as eluant) to yield the title cyclopropachromene (**1**) (5.42 g, 99%) as described above.

3-(*Dichloromethylene*)-7-*methoxy*-2,2-*dimethylchroman*-4-*one* (**2**).—The trichlorocyclopropachromene (**1**) (2.18 g, 7.09 mmol) was dissolved in the minimum of acetonitrile (0.5 ml) and water (1 drop) was added. Silver nitrate (4.82 g, 28.4 mmol) was also added and the reaction mixture was stirred at room temperature for 10 min. A further quantity of silver nitrate (2.41 g, 14.2 mmol) was then added and the mixture stirred vigorously under reflux for 2 h. The mixture was diluted with dichloromethane which was filtered through a little silica gel and the dark solids remaining were extracted with more dichloromethane (3 × 20 ml) which was also filtered. The combined filtrates were concentrated and the residue chromatographed on silica gel (dichloromethane–light petroleum as eluant) to give the title chromanone (**2**) (1.90 g, 93%) as yellow *prisms*, m.p. 104—105 °C (from light petroleum–dichloromethane); $\nu_{max.}$(KBr) 1 672 and 1 611 cm$^{-1}$; $\lambda_{max.}$(EtOH) 211 (ε 21 900 dm$^3$ mol$^{-1}$ cm$^{-1}$), 237sh (10 100), 248 (10 600), 291 (13 400), and 337 nm (11 600); $\delta_H$($CDCl_3$) 1.80 (6 H, s), 3.78 (3 H, s), 6.29 (1 H, d, $J$ 2 Hz), 6.51 (1 H, dd, $J$ 8 and 2 Hz), and 7.69 (1 H, d, $J$ 8 Hz); $\delta_C$($CDCl_3$) 27.51q, 55.65q, 83.24s, 100.96d, 110.32d, 115.18s, 128.72s, 129.22d, 135.45s, 159.91s, 166.42s, and 180.49s) [Found: C, 54.45; H, 4.1%; $m/z$ (f.a.b.) 287 ($M$ + 1), 271, and 251; ($M$ − 15)$^+$ (e.i.) 271.0006. $C_{13}H_{12}Cl_2O_3$ requires C, 54.38; H, 4.21%; $M$, 286; ($M$ − 15) 270.9928].

3-(*Dichloromethylene*)-7-*methoxy*-2,2-*dimethylchroman*-4-*ol* (**5**).—Sodium borohydride (0.245 g, 6.48 mmol) was added to a solution of the 3-(dichloromethylene)chromanone (**2**) (0.189 g, 0.66 mmol) in ethanol (15 ml) and the solution was allowed to stand at room temperature overnight. It was then diluted with water (75 ml) and extracted with ether (4 × 20 ml). The combined extracts were washed with water (2 × 10 ml) and dried ($MgSO_4$). Removal of the solvent left a colourless residue which was chromatographed on silica gel (dichloromethane–light petroleum as eluant) to yield the title chroman-4-ol (**5**) as a colourless *gum* (0.095 g, 50%); $\nu_{max.}$(KBr) 3 469 br, 1 620, 1 592, and 1 504 cm$^{-1}$; δ($CDCl_3$) 1.45 and 1.86 (each 3 H, s), 2.28 (1 H, br), 3.64 (3 H, s), 5.45 (1 H, s, 4-H), 6.46 (1 H, d, $J$ 2 Hz), 6.54 (1 H, dd, $J$ 2 and 8 Hz), and 7.13 (1 H, d, $J$ 8 Hz) (treatment with $D_2O$ caused the signal at δ 2.28 to disappear and that at δ 5.45 to sharpen) (Found: $M^+$, 288.0295. $C_{13}H_{14}Cl_2O_3$ $M$, 288.0320).

The alcohol could not be obtained as crystalline solid; nor could it be acetylated under a variety of conditions in which respect it resembles the corresponding 3-methylenechroman-4-ol obtained previously.[1]

4-(*Dichloromethylene*)-7-*methoxy*-2,2-*dimethylchroman*-3-*yl Acetate* (**7**).—Silver acetate (2.00 g, 12.0 mmol) was added to a solution of the 1,1,7b-trichlorocyclopropachromene (**1**) (0.407 g, 1.15 mmol) in glacial acetic acid (7 ml) containing acetic anhydride (2 drops) and the mixture was stirred under reflux for 36 h. The mixture was cooled and poured into water (100 ml) and the product extracted with dichloromethane (3 × 30 ml). The combined extracts were washed with saturated aqueous sodium hydrogen carbonate (3 × 10 ml), dried ($MgSO_4$), and evaporated to leave a yellow oil which was chromatographed on silica gel (dichloromethane–light petroleum as eluant) to give the title 3-acetoxy derivative (**7**) (0.321 g, 84%) obtained as pale yellow *needles*, m.p. 79 °C (from light petroleum–dichloromethane); $\nu_{max.}$(film) 1 747, 1 617, 1 568, and 1 499 cm$^{-1}$; $\lambda_{max.}$(EtOH) 206 (end abs.) (ε 4 950 dm$^3$ mol$^{-1}$ cm$^{-1}$), 219

(6 450), 237 (4 100), 276 (5 900), and 307 nm (4 100); δ($CDCl_3$) 1.29, 1.43, and 2.00 (each 3 H, s), 3.79 (3 H, s), 5.99 (1 H, s, 3*H*), 6.40 (1 H, d, *J* 2 Hz), 6.52 (1 H, dd, *J* 8 and 2 Hz), and 7.88 (1 H, d, *J* 8 Hz) (irradiation of the signals at δ 1.29 and 1.43 resulted in nuclear Overhauser enhancements of the signal at 5.99 of 12 and 10% respectively) (Found: C, 54.4; H, 4.8%; $M^+$, 330.0410. $C_{15}H_{16}Cl_2O_4$ requires C, 54.40; H, 4.87% *M*, 330.0426).

When carried out at 80 °C this reaction afforded the acetate (**7**) in 15% yield together with the 3-dichloromethylenechroman-4-one (**2**) (51%).

4-(*Dichloromethylene*)-7-*methoxy*-2,2-*dimethylchroman*-3-*ol*.—(a) *By Hydrolysis*. A solution of the 3-acetate (**7**) (0.214 g, 0.605 mmol) and sodium hydrogen carbonate (0.5 g, 6.0 mmol) in methanol (5 ml) and water (5 ml) was kept overnight at room temperature. Methanol was removed by evaporation and the product extracted with dichloromethane (3 × 30 ml). The combined extracts were washed with water (2 × 10 ml), dried ($MgSO_4$), and evaporated to leave a colourless gum which on silica-gel chromatography (dichloromethane–light petroleum as eluant) afforded the title alcohol (0.180 g, 98%) which yielded fine colourless *needles*, m.p. 89—90 °C (from light petroleum); $\nu_{max.}$(KBr) 3 450, 1 617, 1 567, and 1 499 $cm^{-1}$; $\lambda_{max.}$(EtOH) 220 (ε 10 400 $dm^3$ $mol^{-1}$ $cm^{-1}$), 235sh (7 200), 274 (11 200), and 305 nm (6 500); δ($CDCl_3$) 1.20 and 1.52 (each 3 H, s), 1.84 (1 H, br s), 3.73 (3 H, s), 4.62 (1 H, br s), 6.35 (1 H, d, *J* 2 Hz), 6.46 (1 H, dd, *J* 8 and 2 Hz), and 7.85 (1 H, d, *J* 8 Hz) (treatment with $D_2O$ caused the signal at δ 1.84 to disappear and that at δ 4.62 to sharpen) (Found: C, 54.35; H, 4.85%; $M^+$, 288.0313. $C_{13}H_{14}Cl_2O_3$ requires C, 54.19; H, 4.55% *M*, 288.0320).

(b) *By reduction*. The 3-acetate (**7**) (0.211 g, 0.60 mmol) and lithium tetrahydroaluminate (0.228 g, 4 equiv.) in dry ether (50 ml) were boiled under reflux until all starting material had reacted (36 h). The mixture was cooled and treated with methyl formate (2 ml) and then stirred with saturated aqueous ammonium chloride (20 ml). The ethereal layer was separated, washed with water (10 ml), dried ($MgSO_4$), and evaporated to leave a colourless gum which on silica-gel chromatography afforded the above 3-ol (77%).

*Attempted Oxidation of the* 4-*Dichloromethylene*-3-*ol*.—(a) *By activated manganese*(IV) *oxide*. The alcohol (0.030 g) in chloroform (5 ml) was stirred at room temperature with activated manganese dioxide (0.24 g) for 2 days. No reaction was apparent (t.l.c.).

(*b*) By *pyridinium dichromate*. The alcohol (0.030 g) in dichloromethane or pyridine (5 ml) was stirred with pyridinium dichromate at room temperature overnight. No reaction was apparent (t.l.c.).

(c) *By Jones' reagent*. The alcohol (0.030 g) in acetone (2 ml) was treated with Jones' reagent (0.99 equiv.) and the mixture stirred overnight at room temperature. After work-up no required reaction products were detected (t.l.c. and m.s.).

4-(*Dichloromethylene*)-7-*methoxy*-2,2-*dimethylchroman*-3-*yl Nitrate* (**8**).—The 1,1,7b-trichlorocyclopropachromene (**1**) (0.404 g, 1.78 mmol) was dissolved in glacial acetic acid (4 ml) containing silver nitrate (0.19 g, 1.14 mmol). After 15 min more silver nitrate (1.57 g, 9.24 mmol) was added and the mixture was then stirred and boiled under reflux until all the starting material had disappeared (t.l.c.). After being allowed to cool the reaction mixture was poured into water (50 ml) and extracted with dichloromethane (3 × 20 ml). The combined extracts were washed with water (3 × 10 ml) and dried ($MgSO_4$). Removal of the solvent left a yellow oil which on silica-gel chromatography afforded several fractions. The first was the 3-nitrate (**8**) (0.100 g, 25%) obtained as pale yellow *needles*, m.p. 61—62 °C (from light petroleum); $\nu_{max.}$(KBr) 1 646, 1 618, 1 568, 1 500, and 1 280 $cm^{-1}$; $\lambda_{max.}$(EtOH) 204 (end abs.) (ε 14 600 $dm^3$ $mol^{-1}$ $cm^{-1}$), 218 (12 500), 237sh (7 100), 278 (10 400), and 310 nm (7 600); δ($CDCl_3$) 1.29, 1.49, and 3.64 (each 3 H, s), 5.82 (1 H, s, 3-H), 6.12 (1 H, d, *J* 2 Hz), 6.25 (1 H, dd, *J* 8 and 2 Hz), and 7.59 (1 H, d, *J* 8 Hz) (Found: C, 46.65; H, 3.8; N, 4.2%; $M^+$, 333.0154. $C_{13}H_{13}Cl_2NO_5$ requires C, 46.72; H, 3.92; N, 4.19% *M*, 333.0171).

Further fractions consisted of the 3-acetate (**7**) (0.087 g, 25%) and the 3-dichloromethylenechroman-4-one (**2**) (0.157 g, 30%).

*Attempted Hydrolysis or Reduction of the* 3-*Nitrate* (**8**).—(a) *By aqueous methanolic sodium hydrogen carbonate*,. The nitrate (**8**) (0.050 g) was treated as described for the corresponding acetate (**7**). No reaction occurred (t.l.c.).

(b) *By hydrochloric acid*. The nitrate (0.050 g) was stirred under reflux in tetrahydrofuran (5 ml) containing 2M aqueous hydrochloric acid (1.5 ml) for 24 h. No reaction occurred (t.l.c.).

(c) *By reduction with lithium tetrahydroaluminate*. The nitrate (0.050 g) was boiled in ether with an excess of lithium tetrahydroaluminate for 2 days. No reaction occurred (t.l.c.).

(d) *By reduction with Tin*(II) *chloride*. The alcohol (0.050 g) and tin(II) chloride dihydrate (0.081 g) was stirred in ethanol (5 ml) containing concentrated hydrochloric acid (2 ml). After 2 days no reaction had occurred (t.l.c.).

*Attempted Formation of the Nitrate Ester from the Alcohol*.—Concentrated nitric acid was distilled from urea and cooled to 0 °C. A portion (2 ml) containing urea (0.030 g) was added to the alcohol obtained from the acetate (**7**) (0.060 g). After 5 h the mixture was diluted with water and extracted with dichloromethane (3 × 15 ml). The extract was washed with water (2 × 10 ml), dried ($MgSO_4$), and evaporated. Chromatography of the product afforded a 6-nitro derivative as the only isolated product; δ($CDCl_3$) 1.32 and 1.50 (each 3 H, s), 2.3 (1 H, br), 3.81 (3 H, s), 4.65 (1 H, s), 6.24 (1 H, s), and 8.35 (1 H, s) (Found: $M^+$, 333.0192. $C_{13}H_{13}Cl_2NO_5$ requires *M*, 333.0171).

4-*Bromo*-7-*methoxy*-2,2-*dimethylchromene*.—A method analogous to that described for the corresponding 4-chlorochromene[13] was used. To a solution of dry, freshly distilled dimethylformamide (3.87 ml, 50 mmol) and freshly distilled phosphorus oxybromide (prepared by distillation of a mixture of phosphorus pentabromide and diphosphorus pentoxide) (14.35 g, 50 mmol) in dry trichloroethylene (100 ml) at 0 °C was added a solution of 7-methoxy-2,2-dimethylchromanone (6.86 g, 33.3 mmol) in dry trichloroethylene (100 ml). The mixture was heated at 60 °C for 3 h and then concentrated by evaporation. The orange gum remaining was extracted thoroughly with dichloromethane (5 × 30 ml) and the combined extracts were passed through a little alumina before being reconcentrated. The residue was passed through silica gel (dichloromethane as eluant) to give the title 4-bromochromene (9.06 g, 92%) as a colourless *oil* (m.p. around 20 °C); $\nu_{max.}$(film) 1 616, 1 565, and 1 497 $cm^{-1}$; δ($CDCl_3$) 1.39 (6 H, s), 3.69 (3 H, s), 5.71 (1 H, s), 6.23 (1 H, d, *J* 2 Hz), 6.30 (1 H, dd, *J* 2 and 8 Hz), and 7.17 (1 H, d, *J* 8 Hz) (Found: $M^+$, 268.0108. $C_{12}H_{13}BrO_2$ requires *M*, 268.0099).

7b-*Bromo*-1,1-*dichloro*-1a,7b-*dihydro*-5-*methoxy*-2,2-*dimethylcyclopropa*[c]*chromene* (**9**).—(a) *Phase-transfer conditions*. A solution of sodium hydroxide (22.6 g, 0.565 mol) in water (25 ml) was added over 30 min to a vigorously stirred solution of 4-bromo-7-methoxy-2,2-dimethylchromene (2.459 g, 9.12 mmol) in chloroform (30 ml) containing benzyltriethylammonium chloride (115 mg) at room temperature. Stirring was continued until all the starting material had reacted (t.l.c., *ca.* 3 h) and the organic and aqueous phases were then separated. The aqueous layer was extracted with chloroform

(3 × 20 ml) and the combined organic phases were dried ($MgSO_4$), and evaporated. The residue was then chromatographed on silica gel (dichloromethane–light petroleum as eluant). The first material eluted was the title bromocyclopropachromene (**9**) (1.44 g, 45%) obtained as almost colourless *prisms*, m.p. 74 °C (from light petroleum); $\nu_{max.}$(KBr) 1 618, 1 572, and 1 498 $cm^{-1}$; $\lambda_{max.}$(EtOH) 213 (ε 12 800 $dm^3$ $mol^{-1}$ $cm^{-1}$), and 292 nm (3 850); δ($CDCl_3$) 1.35 and 1.61 (each 3 H, s), 2.25 (1 H, s, 1a-H), 3.67 (3 H, s), 6.21 (1 H, d, *J* 2 Hz), 6.44 (1 H, dd, *J* 2 and 8 Hz), and 7.55 (1 H, d, *J* 8 Hz) (Found: C, 44.2; H, 3.7%; $M^+$, 349.9489. $C_{13}H_{13}BrCl_2O_2$ requires C, 44.35; H, 3.72% *M*, 349.9476).

(b) *From sodium trichloroacetate.* Dry sodium trichloroacetate (63.88 g, 0.34 mol) was added over 12 h to a vigorously stirred boiling solution of 4-bromo-7-methoxy-2,2-dimethylchromene (1.786 g, 5.07 mmol) in dry tetrachloroethylene (125 ml) and dry 1,2-dimethoxyethane (50 ml). When all the starting material had reacted (t.l.c.) the reaction mixture was filtered and concentrated to give a brown oil. The crude product was passed down a column of silica gel (dichloromethane–light petroleum as eluant) to yield the title cyclopropachromene (**9**) (2.225 g, 97%) as described above.

*Solvolysis of* 7b-*Bromo*-1,1-*dichloro*-5-*methoxy*-2,2-*dimethylcyclopropa*[c]*chromene* (**9**).—Silver acetate (2.00 g, 12.0 mmol) was added to a solution of the 7b-bromodichlorocyclopropachromene (**9**) (0.465 g, 1.15 mmol) in glacial acetic acid (7 ml) containing acetic anhydride (2 drops) and the mixture was stirred at 80 °C until starting material had disappeared (t.l.c., 27 h). Work-up as above for the formation of the acetate (**7**) from the trichloro compound (**1**) afforded the acetate (**7**) (0.346 g, 91%).

7-*Methoxy*-2,2-*dimethylchroman*-3,4-*dione* (**10**) *and Its Methanolic Hemiacetal.*—The trichlorocyclopropachromene (**1**) (0.768 g, 2.5 mmol) and silver nitrate (2.55 g, 15 mmol) was dissolved in the minimum acetonitrile (or pyridine) (0.5 ml) and the mixture was stirred under reflux for 5 days. The product was extracted with dichloromethane (5 × 10 ml) and the combined extracts were concentrated and then chromatographed on silica gel. A minor fraction appeared to be the ring-contracted ketone (**12**); δ 1.50 (6 H, s), 3.78 (3 H, s), 6.21 (1 H, d, *J* 2 Hz), 6.49 (1 H, dd, *J* 8 and 2 Hz), and 7.50 (1 H, d, *J* 8 Hz); $M^+$, 192. ($C_{11}H_{12}O_3$ requires *M*, 192). The major fraction was eluted with methanol and afforded a colourless gum (0.165 g, 30%) which proved to be a methanolic hemiacetal; δ($CDCl_3$) 1.19, 1.46, 2.97, and 3.67 (each 3 H, s), 4.60 (1 H, s, O*H*), 6.04 (1 H, d, *J* 2 Hz), 6.22 (1 H, dd, *J* 2 and 8 Hz), and 7.41 (1 H, d, *J* 8 Hz) from which methanol could be removed under reduced pressure at 65 °C or by azeotropic distillation with toluene. Removal of methanol left the 3,4-dione (**10**) as a colourless *gum* (0.160 g); δ($CDCl_3$) 1.68 (6 H, s), 3.85 (3 H, s), 6.27 (1 H, d, *J* 2 Hz), 6.49 (1 H, dd, *J* 2 and 8 Hz), and 7.63 (1 H, d, *J* 8 Hz) (Found: $M^+$, 220.0694. $C_{12}H_{12}O_4$ requires *M*, 220.0735).

*Quinoxaline of* 7-*Methoxy*-2,2-*dimethylchroman*-3,4-*dione* (**11**).—The dione (**10**) (0.086 g, 0.39 mmol) was dissolved in glacial acetic acid (10 ml) and to this was added a solution of *ortho*-phenylenediamine (0.042 g, 0.39 mmol) in acetic acid (2 ml). The mixture was boiled gently for 15 min and then cooled and poured into ice–water (50 ml). The mixture was extracted with dichloromethane (4 × 20 ml) and the combined extracts were washed with water (4 × 10 ml), dried ($MgSO_4$), and evaporated to leave a yellow solid. This was passed through a little alumina in dichloromethane and, after concentration, chromatographed on silica gel (dichloromethane–ether as eluant) to give the title quinoxaline (**11**) (0.095 g, 84%) as pale yellow *plates*, m.p. 157 °C (from ethanol); $\nu_{max.}$(KBr) 1 613, 1 586, 1 556, 1 509, and 1 271 $cm^{-1}$; $\lambda_{max.}$(EtOH) 220 (ε 31 800 $dm^3$ $mol^{-1}$ $cm^{-1}$), 249 (16 200), 284 (23 400), and 380 nm (21 000); δ($CDCl_3$) 1.78 (6 H, s), 3.69 (3 H, s), 6.30 (1 H, d, *J* 2 Hz), 6.44 (1 H, dd, *J* 2 and 8 Hz), 7.40 (2 H, br m), 7.70 (2 H, br), and 8.00 (1 H, d, *J* 8 Hz) (Found: C, 73.9; H, 5.4; N, 9.45%; $M^+$, 292.1188. $C_{18}H_{16}N_2O_2$ requires C, 73.95; H, 5.52; N, 9.58%; *M*, 292.1212).

### *Crystal Structure Determinations*

*Crystal Data for* (**2**).—$C_{13}H_{12}Cl_2O_3$, $M_r$ = 287.1, Triclinic, *a* = 8.232(2), *b* = 9.134(2), *c* = 0.540(3) Å, α = 76.60(1), β = 80.64(1), γ = 66.06(1)°, *V* = 635.9 Å$^3$ (from 2θ values of 32 reflections, 20 < 2θ < 25°), *Z* = 2, $D_c$ = 1.500 g $cm^{-3}$, *F*(000) = 296, μ(Mo-$K_\alpha$) = 0.51 $mm^{-1}$, λ = 0.710 73 Å, space group $P\bar{1}$, *T* = 20 °C.

*Data collection and processing.* Stoe-Siemens diffractometer, crystal size 0.35 × 0.38 × 0.46 mm, ω/θ scan mode with one-line profile fitting,[14] $2\theta_{max.}$ 50°, index ranges *h* −9 to 5, *k* −10 to 10, *l* −11 to 11, no variation observed for three standard reflections, no absorption correction; 3 742 reflections measured, 2 233 unique, 1 998 with $F > 4\sigma_c(F)$ ($\sigma_c$ from counting statistics only), $R_{int}$ = 0.016.

*Structure solution and refinement.*[15] Direct methods, blocked-cascade refinement on *F*, weighting[16] $w^{-1} = \sigma^2(F) = \sigma_c^2(F) + 1.8—0.1G + 0.8G^2—3.3S + 1.4S^2 + 1.9GS$, insignificant extinction effects, *R* = 0.046, *wR* = 0.051, 173 parameters, max. shift/e.s.d. 0.018, final difference electron density within ±0.66 eÅ$^{-3}$, slope of normal probability plot 1.04.

*Crystal Data for* (**8**).—$C_{13}H_{13}Cl_2NO_5$, $M_r$ = 334.2, Monoclinic, *a* = 10.609(1), *b* = 8.690(1), *c* = 16.213(1) Å, β = 95.92(1)°, *V* = 1 486.8 Å$^3$ (from 32 reflections, 45 < 2θ < 56°), *Z* = 4, $D_c$ = 1.493 g $cm^{-3}$, *F*(000) = 688, μ(Cu-$K_\alpha$) = 4.2 $mm^{-1}$, λ = 1.541 84 Å, space group $P2_1/n$, *T* = 22 °C.

*Data collection and processing.* Crystal size 0.36 × 0.40 × 0.60 mm, $2\theta_{max.}$ 120°, *h* −11 to 11, *k* 0 to 9, *l* 0 to 18, semi-empirical absorption correction,[15] transmission 0.06—0.19; 2 202 unique reflections, 2 008 with $F > 4\sigma_c(F)$.

*Structure solution and refinement.* As for (**2**), with $w^{-1} = \sigma_c^2(F) + 77 - 790G + 1\,417G^2 - 155S^2 + 749GS$, extinction parameter $x = 3.9(1) \times 10^{-5}$ [$F_c' = F_c/(1 + xF_c^2/\sin 2\theta)^{\frac{1}{4}}$], *R* = 0.061, *wR* = 0.037, 200 parameters, max. shift/e.s.d. 0.003,

**Table 1.** Fractional atomic co-ordinates (× $10^4$) for compound (**2**)

| Atom | *x* | *y* | *z* |
|---|---|---|---|
| Cl(1) | −3 212(1) | 2 838(1) | −1 231(1) |
| Cl(2) | −986(1) | 3 458(1) | −3 650(1) |
| O(1) | −1 183(3) | 1 320(3) | 1 130(2) |
| O(2) | 2 413(2) | 3 438(2) | −354(1) |
| O(3) | 4 433(3) | 2 056(2) | 4 366(2) |
| C(1) | 3 318(2) | 1 181(2) | −1 636(2) |
| C(2) | 1 948(3) | 4 139(3) | −2 771(2) |
| C(3) | 1 904(2) | 2 840(2) | −1 449(2) |
| C(4) | 100(2) | 2 679(2) | −931(2) |
| C(5) | −1 162(2) | 2 963(2) | −1 793(2) |
| C(6) | −90(3) | 1 926(2) | 646(2) |
| C(7) | 1 185(2) | 1 890(2) | 1 568(2) |
| C(8) | 1 187(3) | 1 137(2) | 3 031(2) |
| C(9) | 2 286(3) | 1 206(3) | 3 928(2) |
| C(10) | 3 427(3) | 2 042(2) | 3 385(2) |
| C(11) | 3 470(3) | 2 783(2) | 1 936(2) |
| C(12) | 2 349(2) | 2 678(2) | 1 043(2) |
| C(13) | 5 591(4) | 2 912(4) | 3 906(3) |

**Table 2.** Fractional atomic co-ordinates ( $\times 10^4$) for compound (**8**)

| Atom | *x* | *y* | *z* |
|---|---|---|---|
| Cl(1) | 6 257(1) | 2 121(1) | 4 346(1) |
| Cl(2) | 4 435(1) | 1 726(1) | 2 941(1) |
| N | 1 642(4) | −262(4) | 4 150(3) |
| O(1) | 1 625(3) | 1 220(3) | 4 498(1) |
| O(2) | 2 200(4) | −455(4) | 3 545(2) |
| O(3) | 1 042(4) | −1 136(3) | 4 530(2) |
| O(4) | 1 942(3) | 4 199(3) | 5 157(1) |
| O(5) | 4 218(3) | 4 128(3) | 7 821(1) |
| C(1) | 4 665(4) | 2 043(4) | 4 009(2) |
| C(2) | 3 725(3) | 2 260(3) | 4 468(2) |
| C(3) | 2 393(4) | 2 352(3) | 4 097(2) |
| C(4) | 1 850(4) | 3 925(4) | 4 268(2) |
| C(5) | 2 600(5) | 5 125(4) | 3 863(2) |
| C(6) | 450(4) | 4 038(5) | 3 994(2) |
| C(7) | 2 982(4) | 3 645(3) | 5 636(2) |
| C(8) | 3 049(4) | 4 166(4) | 6 469(2) |
| C(9) | 4 042(4) | 3 657(4) | 7 015(2) |
| C(10) | 4 914(4) | 2 622(4) | 6 757(2) |
| C(11) | 4 829(4) | 2 138(4) | 5 951(2) |
| C(12) | 3 862(4) | 2 671(3) | 5 354(2) |
| C(13) | 3 337(4) | 5 223(5) | 8 106(2) |

final difference electron density within $\pm 0.31$ eÅ$^{-3}$, slope of normal probability plot 1.27.

Atomic co-ordinates for both structures are given in Tables 1 and 2. Full crystallographic data are available from the Cambridge Crystallographic Data Centre.*

* See Instructions for Authors (1990), *J. Chem. Soc., Perkin Trans. 1*, 1990, Issue 1.

## References


1 Part 7. P. Anastasis, P. E. Brown, and W. Y. Marcus, *J. Chem. Res.* 1989, (*M*), 429; (*S*), 36.

2 P. E. Brown and Q. Islam, *Tetrahedron Lett.*, 1987, **28**, 3047.

3 J. D. Roberts and V. C. Chambers, *J. Am. Chem. Soc.*, 1951, **73**, 5034; C. H. DePuy, L. G. Schnack, and J. W. Hausser, *ibid.*, 1966, **88**, 3343; W. F. Sliwinski, T. M. Su, and P. v. R. Schleyer, *ibid.*, 1972, **94**, 133; R. B. Woodward and R. Hoffmann, *ibid.*, 1965, **87**, 395.

4 C. H. DePuy, F. W. Breitbeil, and K. R. DeBruin, *J. Am. Chem. Soc.*, 1966, **88**, 3347; C. H. DePuy, *Acc. Chem. Res.*, 1968, **1**, 33; D. H. Gibson and C. H. DePuy, *Chem. Rev.*, 1974, **74**, 605; A. DeBoer and C. H. DePuy, *J. Am. Chem. Soc.*, 1970, **92**, 4008; T. C. Macdonald and R. Dolan, *J. Org. Chem.*, 1979, **44**, 4973.

5 H. C. Brown, C. G. Rao, and M. Ravindranathan, *J. Am. Chem. Soc.*, 1977, **99**, 7663; H. C. Brown, C. G. Rao, and M. Ravindranathan, *ibid.*, 1978, **100**, 7946.

6 J. Salaün, *J. Org. Chem.*, 1976, **41**, 237; 1977, **42**, 28; 1978, **43**, 2809.

7 J. A. Landgrebe and L. W. Becker, *J. Am. Chem. Soc.*, 1967, **89**, 2505; R. A. Martin and J. A. Landgrebe, *J. Org. Chem.*, 1972, **37**, 1996.

8 L. Radom, P. C. Hariharan, J. A. Pople, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, 1973, **95**, 6531; D. B. Ledlie and E. A. Nelson, *Tetrahedron Lett.*, 1969, 1175; E. Jongejan, W. J. M. van Tilborg, C. H. V. Dussen, H. Steinberg, and T. J. deBoer, *ibid.*, 1972, 2359; U. Schöllkopf, E. Ruban, P. Tonne, and K. Riedel, *ibid.*, 1970, 5077; C. W. Jefford, *Chimia*, 1970, **24**, 357; R. Jorritsman, H. Steinberg, and T. J. deBoer, *Recl. Trav. Chim. Pays-Bas*, 1981, **190**, 194; B. A. Howell and J. G. Jewett, *J. Am. Chem. Soc.*, 1971, **93**, 798.

9 J. A. Berson and S. S. Olin, *J. Am. Chem. Soc.*, 1970, **92**, 1087; W. Kirmse and H. Schütte, *Chem. Ber.*, 1968, **101**, 1674; S. J. Cristol, R. M. Sequeira, and C. H. DePuy, *J. Am. Chem. Soc.*, 1965, **87**, 4007; P. v. R. Schleyer, G. W. VanDine, U. Schöllkopf, and J. Paust, *ibid.*, 1966, **88**, 2868; X. Creary, *J. Org. Chem.*, 1975, **40**, 3326; L. Skattebøl, *ibid.*, 1966, **31**, 1554; S. R. Sandler, *ibid.*, 1968, **33**, 4537; D. T. Clark and G. Smale, *J. Chem. Soc., Chem. Commun.*, 1969, 1050; X. Creary, *J. Org. Chem.*, 1976, **41**, 3734 and 3740; X. Creary, M. Keller, and J. P. Dinnocenzo, *ibid.*, 1978, **43**, 3874; C. B. Reese and M. R. D. Steebles, *Tetrahedron Lett.*, 1972, 4427; M. S. Baird and P. D. Slowey, *ibid.*, 1982, 3795; M. G. Banwell and J. H. Knight, *J. Chem. Soc., Chem. Commun.*, 1987, 1082.

10 L. A. Paquette, *Acc. Chem. Res.*, 1971, **4**, 280; Z. Majerski and K. Mlinarić-Majerski, *J. Org. Chem.*, 1986, **51**, 3219; M. R. A. Blomberg, P. E. M. Siegbahn, and J.-E. Bäckvall, *J. Am. Chem. Soc.*, 1987, **109**, 4450; D. B. Collum, F. Mohamadi, and J. S. Hallock, *ibid.*, 1983, **105**, 6882; I. Ryu, K. Matsumoto, M. Ando, S. Murai, and N. Sonoda, *Tetrahedron Lett.*, 1980, 4283; I. Ryu, M. Ryang, I. Rhee, H. Omura, S. Murai, and N. Sonoda, *Synth. Commun.*, 1984, **14**, 1175.

11 B. Giese and W. Zwick, *Chem. Ber.*, 1979, **112**, 3766; 1982, **115**, 2526; 1983, **116**, 1264.

12 G. M. Blackburn and C. R. M. Ward, *J. Chem. Soc., Chem. Commun.*, 1976, 80.

13 P. Anastasis, P. E. Brown, and W. Y. Marcus, *J. Chem. Soc., Perkin Trans. 1*, 1985, 1127.

14 W. Clegg, *Acta Crystallogr., Sect. A*, 1981, **37**, 22.

15 G. M. Sheldrick, 'SHELXTL, an integrated system for solving, refining and displaying crystal structures from diffraction data. Revision 5. University of Göttingen, 1985.

16 W. Hong and B. E. Robertson, 'Stucture and Statistics in Crystallography,' ed. A. J. C. Wilson, Academic Press, New York, 1985, p. 125.


*Received* 30*th May* 1989; *Paper* 9/02248A