Reactions of Co-ordinated Ligands. Part 10.[1] Rhodium-catalysed Cyclisation of 3-(2-Fluorophenyl)propanols to Chromans

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The cyclisation of several 3-(2-fluorophenyl)-propanols to the corresponding chroman occurs in nitromethane–acetone solution at 80 °C when either the hexafluorophosphate (**3**) or tetrafluoroborate salt (**4**) of the (η^5-ethyltetramethylcyclopentadienyl)(η^6-benzene)rhodium(III) cation is used as a catalyst; the former salt is the more effective catalyst. The cyclisation is believed to involve the activation of the aryl fluoride (towards intramolecular nucleophilic substitution by the hydroxy group) by the formation of a metal complex in which the aryl fluoride is π-bonded with the metal cation. It is suggested that the arene-exchange reaction which gives this π-bonded complex proceeds faster with the salt (**3**) than with the salt (**4**), and that this is the main factor for the greater efficiency of the former salt as a cyclisation catalyst.

In the previous Paper[1] in this Series it was shown that treatment of the tricarbonylchromium complex of 3-(2-fluorophenyl)-propanol with metal alkoxides initiated an intramolecular nucleophilic substitution and gave the tricarbonylchromium complex of chroman from which the heterocycle was liberated by mild oxidation. In order for this type of reaction to be modified so that it provided a convenient and general synthesis of chromans it was thought necessary to replace the tricarbonylchromium residue by an alternative metal/ligand combination which would (*a*) activate the aryl fluoride to an extent which would allow the intramolecular nucleophilic substitution to proceed in the absence of added base, *i.e.* the nucleophilic centre would then be a neutral hydroxy group rather than the alkoxide anion generated from it, and (*b*) be readily transferred from the arene ring of the cyclised product to that of the unchanged starting material, thus allowing the cyclisation to be metal-catalysed as distinct from metal-promoted. As indicated in our preliminary communication,[2] we found that both these requirements appeared to be met by the (η^5-ethyltetramethylcyclopentadienyl)rhodium(III) cation which was generated *in situ* from the η^6-benzene complex (**2**).

$[Rh(\eta^5\text{-}C_5EtMe_4)Cl_2]_2$ (**1**)

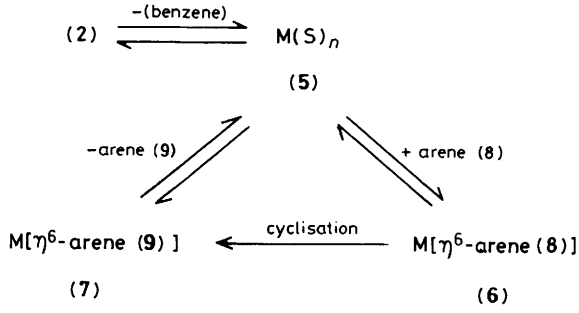
$[Rh(\eta^5\text{-}C_5EtMe_4)(\eta^6\text{-benzene})]^{2+}$ (**2**)

$[(2)][X^-]_2$

(**3**) X = PF_6
(**4**) X = BF_4

This complex was found to catalyse the cyclisation of fluoro alcohols of type (**8**) to the corresponding chroman (**9**) under relatively mild conditions and was thought to act as shown in the Scheme. Here we report details of this work.

As described by White and his co-workers,[3] addition of silver hexafluorophosphate(v) to the dimer (**1**) in acetone gave a solution of the species (**5**; S = acetone) which was converted into the benzene complex (**2**) *in situ* by addition of an excess of benzene. This complex was isolated from the reaction mixture in the form of its hexafluorophosphate salt (**3**); the tetrafluoroborate salt (**4**) was obtained in an analogous manner. The ^1H n.m.r. spectra of both salts (in [$^2H_3$]nitromethane) showed a signal due to co-ordinated benzene (δ 7.46) and a signal due to the four methyl groups attached to the five-membered ring (δ 2.33). With salts of the analogous (η^5-pentamethylcyclopentadienyl)(η^6-arene)rhodium(III) cation the position of the signal due to the five methyl groups has been shown by Maitlis and his co-workers[4] to be dependent on the arene, and in the case of benzene occurs at δ 2.45 (in [$^2H_6$]acetone). A similar dependency was observed in the present work and (as described below) conversion of the benzene complex (**2**) into chroman complexes of type (**7**) was always accompanied by an upfield shift (by *ca.* 0.1 p.p.m.) of the signal at δ 2.33.



Scheme. M = $[Rh(\eta^5\text{-}C_5EtMe_4)]^{2+}$ and S = σ-bonded ligand, *e.g.* a molecule of solvent or alcohol (**8**)

	R^1	R^2
a;	H	H
b;	Me	H
c;	H	CH_2OH
d;	H	o-FC_6H_4·CH_2

The ^1H n.m.r. spectra of solutions of the two salts in [$^2H_3$]nitromethane were unchanged after the solutions had been heated at 40 °C for 4 h, indicating that there was no displacement of the co-ordinated benzene by the nitromethane. In contrast, when the hexafluorophosphate salt was briefly warmed with [$^2H_6$]dimethyl sulphoxide or with [$^2H_4$]methanol

the ^{1}H n.m.r. spectra of the resultant solutions indicated that the benzene had been displaced completely and that solvated species of type (**5**) had been formed. In both cases the signal due to the benzene was at δ 7.34, and the signal originally at δ 2.33 had moved upfield (δ 1.53, [$^2H_6$]dimethyl sulphoxide; δ 1.65, [$^2H_4$]methanol). Here also, Maitlis and his co-workers[4] have observed that in the ^{1}H n.m.r. spectra of solutions which contain cations of the type (η^5-pentamethylcyclopentadienyl)-(solvent)$_n$rhodium(III) the position of the signal due to the five methyl groups is dependent on the solvent co-ordinated with the metal and can vary from δ 1.85 (acetone) to δ 1.52 (pyridine). It was also observed that in some cases (solvent = acetonitrile, dimethyl sulphoxide, pyridine) the cations could be isolated as stable hexafluorophosphate salts, but in others (solvent = acetone, methanol, dichloromethane) this was not possible. In the present work all attempts to isolate the salt [Rh(η^5-C_5EtMe_4)(methanol)$_n$][PF_6]$_2$ were unsuccessful.

In order to study the displacement of the benzene from the salt (**3**) a solution of the salt (5.7×10^{-2}M) and methanol (0.29M) in [$^2H_3$]nitromethane was heated at 80 °C and the reaction was followed by ^{1}H n.m.r. spectroscopy.* After 24 h of heating *ca.* 55% of the benzene had been displaced. In complete contrast, no displacement of benzene occurred when the tetrafluoroborate salt (**4**) was heated under identical conditions for 48 h. An even greater contrast between the behaviour of the two salts was observed when they were heated at 80 °C in an acetone–nitromethane mixture (see below) with the nitro alcohol (**12**)—which did not undergo cyclisation to the corresponding chroman under these conditions (also see below). Whereas the co-ordinated benzene in the salt (**3**) was completely displaced after 3 h of heating, no detectable amount of displacement of benzene was observed when the tetrafluoroborate salt (**4**) was heated under identical conditions for 1 week. These observations are very similar to those made by Sievert and Muetterties[5] (and reported after the publication of our preliminary communication) in their study of the arene-exchange reaction between the cyclo-octadiene (COD) complex [Ir(η^6-*p*-xylene)(η^4-COD)]$^+$ and polymethylated benzenes such as 1,2,3,4-tetramethylbenzene. They found that in chloroform at room temperature and a reaction time of 382 h, extensive exchange occurred when the complex was used as its trifluoromethanesulphonate salt, but no exchange occurred with the tetrafluoroborate salt. It was suggested that this difference arose because with the former salt the anion could participate in the exchange by displacing the *p*-xylene to form a σ-bonded sulphonato complex. It is possible that a similar process operates in the rhodium(III) system described here, and that with the hexafluorophosphate salt either fluoride or other species formed by alcoholysis or adventious hydrolysis[6,7] of the PF_6 anion promote the displacement of the benzene from the metal. If this is so, then it follows that the ^{1}H n.m.r. signal in the region of δ 1.5 which appears on displacement of the benzene could be due, at least in part, to metal complexes in which the ethyltetramethylcyclopentadienylrhodium(III) residue is σ-bonded to inorganic anion(s) as well as to solvent molecules. Support for these suggestions is provided by the observation made very recently[8] when a solution in nitromethane of the hexafluorophosphate salt (6×10^{-2}M) and methanol (1.2M) was heated at 80 °C for 4 h. Not only did the ^{1}H n.m.r. spectrum of the resultant solution show that the benzene had been displaced from the metal (δ 7.34 and 1.65), but the ^{31}P and ^{19}F n.m.r. spectra indicated that all the hexafluorophosphate anion had been converted into dimethyl phosphorofluoridate [$(MeO)_2P(O)F$]. No changes in either the ^{1}H or ^{19}F n.m.r. spectra were observed when the experiment was repeated using the tetrafluoroborate salt (**4**).

Displacement of the co-ordinated benzene from the hexafluorophosphate salt (**3**) was also observed when equimolar amounts of the salt and the fluoro alcohol (**8a**) in [$^2H_3$]nitromethane were heated at 80 °C. However, the disappearance of the signal at δ 2.33 was accompanied not only by the expected appearance of signal at δ 1.57 but also by the appearance of a signal at δ 2.25 whose intensity steadily increased with heating. This increase in intensity was also accompanied by (*a*) a slight upfield shift of some of the signals due to the aromatic protons, (*b*) a progressive decrease in the intensity of the triplet at δ 3.61 (CH_2·OH), and (*c*) the appearance of a triplet at δ 4.10. All these changes were consistent with cyclisation of the fluoro alcohol (**8a**) to chroman, which presumably was present in the reaction mixture both as the free heterocycle and as a π-complex of type (**7**) with the latter species being responsible for the signal at δ 2.25. After 17 h of heating the relative intensity of the signals at δ 3.61 and 4.10 (CH_2·OAr) indicated that cyclisation had occurred to the extent of *ca.* 65%. When the experiment was repeated using a 17% (v/v) solution of acetone in [$^2H_3$]nitromethane as the solvent almost complete cyclisation occurred during 20 h of heating, but in contrast no evidence of cyclisation was obtained (after 17 h) when either dioxane or dimethylformamide were used as solvents under reflux conditions or when 2-methylpyridine was added to the reaction mixture with acetone–[$^2H_3$]nitromethane as the solvent.

Proof that the hexafluorophosphate salt could actually *catalyse* the cyclisation of the fluoro alcohol (**8a**) to chroman was obtained when a solution of the salt (4.6×10^{-2}M) and the fluoro alcohol (28×10^{-2}M) in [$^2H_3$]nitromethane which contained 20% (v/v) of acetone was heated at 80 °C for 24 h. The ^{1}H n.m.r. spectrum of the resultant mixture indicated that cyclisation had occurred to the extent of *ca.* 55%. Addition of dimethyl sulphoxide to the mixture followed by heating at 80 °C for 1 h [in order to displace the chroman from the complex of type (**7**)] resulted in the subsequent isolation of a mixture of unchanged fluoro alcohol and chroman which was resolved by column chromatography on alumina.

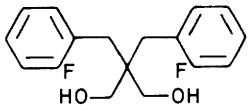
The tetrafluoroborate salt (**4**) also catalysed the cyclisation of the fluoro alcohol (**8a**) but was less effective than the hexafluorophosphate one: under the conditions specified immediately above the degree of cyclisation was *ca.* 30%. Significantly, at no stage during the 24 h of heating with the tetrafluoroborate salt did the ^{1}H n.m.r. spectrum of the reaction mixture show a signal in the region of δ 1.5. Also, at corresponding intervals of time the intensity of the signal at δ 2.25 was far stronger than when the hexafluorophosphate salt had been used, indicating that the chroman complex of type (**7**) was present at a much higher concentration in the tetrafluoroborate system even though the degree of cyclisation was lower. These three differences between the effects of the hexafluorophosphate and tetrafluoroborate salts were also observed when the two salts were used to catalyse the cyclisation of the fluoro alcohols (**8c** and **d**) and (**10**) in the acetone–[$^2H_3$]nitromethane mixture at 80 °C: in every case the cyclisation proceeded at a faster rate than the corresponding cyclisation of the unsubstituted fluoro alcohol (**8a**) [see Table and also note the high preparative yield of the previously unknown spiro compound (**11**)]. With the secondary alcohol (**8b**), however, although the rate of cyclisation with the hexafluorophosphate salt was faster than with the tetrafluoroborate salt, no ^{1}H n.m.r. signal in the region of δ 1.5 was observed, and with both salts the relative intensity of the n.m.r. signal at δ 2.25 roughly paralleled the degree of cyclisation.

* In the present work all the reaction mixtures (*ca.* 0.5 ml) kept at 80 °C were contained in stoppered glass tubes (18 cm long) which were held vertically and which were heated only along that portion of the tube which contained the reaction mixture. Under these conditions very little loss of volatile material occurred, even during many days of heating.

Table. Rhodium-catalysed conversion of fluoro alcohols into chromans

Fluoro alcohol	(8a)	(8b)	(8c)	(8d)	(10)	(13)
Chroman	9a	9b	9c	9d	11	6-Methoxychroman
Conversion (%) with salt (3)[a]	55	55	75	80	90	35
Conversion (%) with salt (4)[a]	30	30	65	65	80	20
Isolated yield (%) of chroman[b]	25[c]	48[c]	82	85	90	48[c]

[a] Calculated (to the nearest 5%) from the ^{1}H n.m.r. spectrum obtained after a solution of the salt (4.6×10^{-2}M) and the fluoro alcohol (28×10^{-2}M) in [$^2H_3$]nitromethane which contained 20% (v/v) of acetone had been heated at 80 °C for 24 h. [b] Using the preparative procedure described in the Experimental section. [c] Based on recovered fluoro alcohol.



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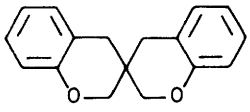

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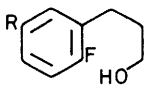
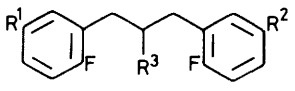
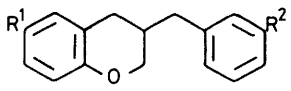


(12) R = NO_2
(13) R = MeO

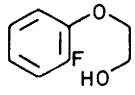
The effect of nuclear substituents on the rate of cyclisation was examined using the fluoro alcohols (**12**) and (**13**). With the former alcohol no evidence of cyclisation was observed with either the hexafluorophosphate or tetrafluoroborate salt (or in the absence of both salts) when the reaction mixtures were heated at 80 °C for 13 days. With the methoxy compound, however, the cyclisation proceeded in the expected manner with the hexafluorophosphate being the more effective of the two salts; however in both cases the cyclisation was slower than the corresponding cyclisation with the parent fluoro alcohol (**8a**) (see Table). This retarding effect of the methoxy group was also observed in the cyclisation of the mixed system (**14**). With both the hexafluorophosphate and tetrafluoroborate salt (again, the former was the more effective) the ^{1}H n.m.r. signal at δ 3.68 due to the methoxy group in the starting material was slowly replaced during 24 h of heating by two signals at δ 3.72 and 3.64 which were assigned to the methoxy groups in the chromans (**16**) and (**17**) respectively, and whose intensities were in the ratio 7:3.



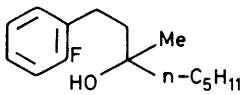
(14) R^1 = H, R^2 = OMe
R^3 = CH_2OH
(15) R^1 = R^2 = H R^3 = CO_2H



(16) R^1 = H, R^2 = OMe
(17) R^1 = OMe, R^2 = H



(18)



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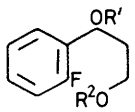
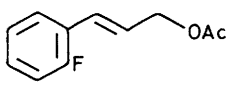


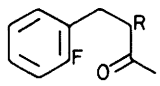
(20) R^1 = H, R^2 = CH_2Ph
(21) R^1 = COMe, R^2 = CH_2Ph
(22) R^1 = COMe, R^2 = H



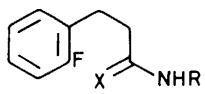
(23)

The results with the fluoro alcohol (**18**) were anomalous. With the hexafluorophosphate salt as catalyst and a reaction period of 4 days no changes were observed in the ^{1}H n.m.r. spectrum after the initial displacement of benzene (complete within 1 h). With the same reaction time, however, the tetrafluoroborate salt effected cyclisation to the benzodioxane to the extent of *ca.* 25%, and this figure slowly increased to 35% after a further 9 days of heating.

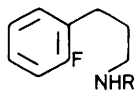
Attempts to cyclise the alcohols (**19**) and (**22**) using the two salts were unsuccessful. The former alcohol gave (with both salts) a mixture of products the ^{1}H n.m.r. spectrum of which was identical with that of the mixture obtained by dehydrating the alcohol with toluene-*p* sulphonic acid; the latter alcohol gave (again, with both salts) a product which on the basis of spectroscopic data appeared to be the allylic acetate (**23**). Although these products are consistent with the involvement of those acid-catalysed reactions which would be expected to take place as the result of the formation of hydrogen fluoride by cyclisation of the fluoro alcohols, no cyclisation product was detected (^{1}H n.m.r.) in any of the experiments. The effect of the two salts (**3**) and (**4**) in [$^2H_3$]nitromethane at 80 °C on the ketones (**24**) and (**25**), the carboxylic acid (**15**), and the amides (**26**), (**27**), and (**28**), was also examined, but with these systems again no evidence of cyclisation was obtained. This was also the case when attempts were made to cyclise the amines (**29**) and (**30**) using [Rh(η^5-C_5EtMe_4)(MeCN)$_3$][PF_6]$_2$ as the catalyst.[4]



(24) R = H
(25) R = CO_2Et



(26) R = H, X = O
(27) R = CMe_3, X = O
(28) R = H, X = S



(29) R = H
(30) R = Et

Although it has been suggested that the rhodium-catalysed cyclisations described in this Paper might occur by an electron-transfer chain mechanism,[9] we consider that they proceed by the route outlined in the Scheme, in which the aryl fluoride is activated towards intramolecular nucleophilic substitution by formation of the π-bonded species (**6**). Although there was never any indication in the ^{1}H n.m.r. spectra of the formation of this species, this is not unexpected. On the basis of studies which have been made on the arene-exchange reactions,[10] one would predict that the equilibrium position between the species (**2**), (**5**), and (**6**) would be biased against the last on account of the strong

electron-withdrawing properties of the fluorine atom.* Furthermore, the co-ordination of the aryl fluoride with the highly-charged rhodium cation in the species (**6**) would probably cause this species to be rapidly converted into a chroman complex of type (**7**).

Presumably, the cyclisations proceed faster when acetone is included in the reaction mixtures because this σ-donor ligand in some way assists the arene-exchange reactions which are involved—as observed by Sievert and Meutterties[5] with the iridium(I) system described earlier. We suggest that the arene-exchange reactions are also assisted by those σ-donor ligands which appear to be formed by reaction or decomposition of the hexafluorophosphate anion, and that this is the main reason why the hexafluorophosphate salt is more effective as a cyclisation catalyst than the tetrafluoroborate one. Both the inhibiting effect of 2-methylpyridine on the cyclisation of the fluoro alcohol (**8a**) and the failure of compounds such as (**26**) and (**28**) to undergo cyclisation may be ascribed to the high stability which these strong σ-donors bestow on the species (**5**), thereby drastically reducing the rate at which the π-bonded species (**6**) is formed. In this context it should be noted that whereas in the cyclisation of all the fluoro alcohols the benzene was slowly displaced from the cation (**2**) on heating, in the attempts to cyclise the amides (**26**)—(**28**) the displacement occurred at room temperature, and after 5 min was complete with (**26**) and (**28**) and *ca.* 50% complete with the sterically hindered system (**27**). Although dioxane and dimethylformamide are not such strong σ-donors as the amides just referred to, when used as the solvent their effective concentration would also ensure that the rhodium was present largely in the form of the σ-bonded species (**5**), thereby inhibiting the reaction as observed. This suggestion is supported by the observation that when a solution of fluorobenzene (0.4M), methanol (2.4M), and the hexafluorophosphate salt (**3**) (5.7×10^{-2}M) in [$^2H_3$]nitromethane was heated at 80 °C for 4 days, the fluorobenzene was completely converted (^{1}H n.m.r.) into anisole; when the fluorobenzene and hexafluorophosphate salt was however heated in [$^2H_4$]methanol alone no conversion was observed.

The observed effects of nitro and methoxy substituents on the rate of cyclisation may also be rationalised in terms of equilibrium between the species (**5**) and (**6**). In the former case the presence of the nitro group on the arene ring would cause the equilibrium to be displaced considerably towards the solvated species (**5**), and while a methoxy group would be expected to have the reverse effect (albeit to a much smaller extent)[9] it would appear from the reduced rate of cyclisation that the effect of increasing the relative stability of the species (**6**) is more than reversed by the electronic effect which the methoxy group has on the rate constant of the cyclisation (**6**) ⟶ (**7**).[11]

We are unable to provide a convincing explanation as to why the cyclisation of the fluoro alcohol (**18**) proceeds at a very much slower rate than that of the methoxy compound (**13**) when the tetrafluoroborate salt is used, or why the cyclisation does not seem to proceed at all with the hexafluorophosphate salt. Possibly the explanation for both these anomalies lies in the chelating nature of the side-chain, and its stabilising effect on the species (**5**).

All the aryl fluorides mentioned in this Paper were prepared by standard methods which are detailed in the Experimental section.

* When the acid (**15**) was heated with the tetrafluoroborate salt (**4**) under the usual conditions *ca.* 65% of the benzene was displaced after 6 days. This displacement was associated with the appearance of a ^{1}H n.m.r. signal at δ 2.40, which might be due to a species in which one of the arene rings of the acid was π-bonded to the $[(\eta^5\text{-}C_5EtMe_4)Rh]^{2+}$ cation.

Experimental

^{1}H N.m.r. spectra were recorded on a Perkin-Elmer R32 (90 MHz) instrument with $SiMe_4$ as internal standard and unless stated otherwise, for solutions in $CDCl_3$. Mass spectra were recorded with Varian CH 5D and Finnigan 4000 instruments. I.r. spectra were measured on a Pye Unicam SP 200 spectrometer. Ether refers to diethyl ether throughout. Light petroleum refers to the fraction with b.p. 40—60 °C.

The salts (**3**) and (**4**),[3] the aryl fluorides (**8a**),[1] (**18**),[12] and (**25**)[13] were prepared by the methods described in the literature.

(2-Fluoro-5-methoxyphenyl)methyl Bromide.—This *bromide* was prepared (64% yield) using the method described for the 4-methoxy isomer,[14] and had b.p. 130—138 °C/18 mmHg; δ 6.95—6.65 (3 H, m, ArH), 4.42 (2 H, s, CH_2Br), and 3.76 (3 H, s, CH_3) (Found: C, 43.4; H, 3.5%; M^+, 219. C_8H_8BrFO requires C, 43.9; H, 3.7%; *M*, 219).

Diethyl 1,3-*Bis*(2-*fluorophenyl*)*propane*-2,2-*dicarboxylate.*—Diethyl malonate (12.8 g, 80 mmol) followed by 2-fluorobenzyl bromide (30 g, 156 mmol) was added to sodium ethoxide (from sodium, 3.6 g), in dry ethanol (80 ml) and the mixture was stirred and refluxed for 16 h. The bulk of the ethanol was removed by distillation, and a mixture of water (50 ml) and ether (150 ml) was added to the residue. The ether layer was separated, dried, and fractionated to give the *diester* (21.2 g, 57%), b.p. 145—160 °C/0.5 mmHg, which solidified with time and then had m.p. 50—53 °C; $\nu_{max.}$ 1 725 cm^{-1}; δ 7.5—6.8 (8 H, m, ArH), 4.06 (4 H, q, OCH_2), 3.29 (4 H, s, $ArCH_2$), and 3.1 (6 H, t, CH_3) (Found: C, 67.2; H, 5.8%; M^+, 376. $C_{21}H_{22}F_2O_4$ requires C, 67.04; H, 5.85%; *M*, 376).

Diethyl 2-(2-*Fluorophenyl*)*ethane*-1,1-*dicarboxylate.*—The preceding experiment was repeated using twice the quantity of diethyl malonate. The *diester* (24.3 g, 62%) obtained had b.p. 100—110 °C/1.5 mmHg; $\nu_{max.}$ 1 735 cm^{-1}; δ 7.35—6.83 (4 H, m, ArH), 4.12 (4 H, q, 2 × OCH_2), 3.71 (1 H, t, CH_2CH), 3.22 (2 H, d, $ArCH_2$), and 1.17 (6 H, t, 2 × CH_3) (Found: C, 63.05; H, 6.7%; M^+, 268. $C_{14}H_{17}FO_4$ requires C, 62.7; H, 6.4%; *M*, 268).

Diethyl 2-(2-*Fluoro*-5-*methoxyphenylmethyl*)*ethane*-1,1-*dicarboxylate.*—This *diester* was prepared in 58% yield from diethyl malonate (55 mmol), sodium ethoxide (from sodium, 55 mmol), and 2-fluoro-5-methoxybenzyl bromide (55 mmol) using the procedure described above, and had b.p. 140—154/0.75 mmHg; $\nu_{max.}$ 1 740 cm^{-1}; δ 6.87—6.45 (3 H, m, ArH), 4.11 (4 H, q, 2 × OCH_2), 3.69 (4 H, OCH_3 and CH_2CH), 3.13 (2 H, d, $ArCH_2$), and 1.17 (6 H, t, 2 × CH_3) (Found: C, 59.6; H, 6.3%; M^+, 298. $C_{15}H_{19}FO_5$ requires C, 60.4; H, 6.4%; *M*, 298).

Bis(2-*fluorophenylmethyl*)*acetic Acid.*—A mixture of diethyl 1,3-bis(2-fluorophenyl)propane-2,2-dicarboxylate (7 g), potassium hydroxide (4 g), and water (4 ml) was heated under reflux for 16 h and then diluted with a solution of concentrated sulphuric acid (3.5 ml) in water (9 ml). Extraction with ether afforded the *acid* (3.3 g, 64%), m.p. 104—106 °C (ethyl acetate–light petroleum); $\nu_{max.}$ 1 705 cm^{-1}; δ 10.8 (1 H, s, CO_2H), 7.4—6.8 (8 H, m, ArH), and 2.95 (5 H, m, CH_2CHCH_2) (Found: C, 69.3; H, 5.4; M^+, 276. $C_{16}H_{14}F_2O_2$ requires C, 69.6; H, 5.1%; *M*, 276). The following acids were also obtained by hydrolysis of the appropriate diethyl ester with aqueous potassium hydroxide.

3-(2-Fluorophenyl)propanoic acid (78%), m.p. 63—67 °C (lit.,[15] m.p. 82 °C); δ 10.68 (1 H, s, CO_2H), 7.10 (4 H, m, ArH), 2.97 (2 H, t, $ArCH_2$), and 2.66 (2 H, t, CH_2CO) (Found: C, 64.2; H, 5.4%; M^+, 168. Calc. for $C_9H_9FO_2$: C, 64.3; H, 5.4%; *M*, 168).

3-(2-Fluoro-5-methoxyphenyl)propanoic acid obtained in 32% yield as a brown solid, δ10.46 (1 H, s, CO_2H), 7.0—6.4 (3 H, m, ArH), 3.66 (3 H, s, CH_3), and 3.3—2.4 (4 H, m, CH_2CH_2).

2-Fluorophenylmethyl-(2-fluoro-5-methoxyphenylmethyl)-acetic acid was obtained in 59% yield from the crude diester afforded by alkylation of diethyl 2-(2-fluorophenylmethyl)-ethane-1,1-dicarboxylate (38 mmol) by 2-fluoro-5-methoxybenzyl bromide in the presence of sodium ethoxide (from sodium, 38 mg-atom) in dry ethanol (30 ml). The acid had m.p. 69.5—72.5 °C (from light petroleum–toluene), $\nu_{max.}$ 1 710 cm^{-1}; δ 10.48 (1 H, s, CO_2H), 7.3—6.5 (7 H, m, ArH), 3.6 (3 H, s, CH_3), 3.28 (1 H, m, CHCO), and 2.86 (4 H, 2 × $ArCH_2$).

2,2-*Bis*(2-*fluorophenylmethyl*)*ethanol* (**8d**).—Bis(2-fluorophenylmethyl)acetic acid (3.3 g) in dry ether (20 ml) was added dropwise with stirring to lithium aluminium hydride (0.4 g) in dry ether (20 ml). The mixture was stirred for a further 1 h and then the organic material was isolated in the usual manner and fractionated to give the *alcohol* (3.0 g, 96%), b.p. 140—144 °/1 mmHg; $\nu_{max.}$ 3 500 cm^{-1}; δ 7.4—6.8 (8 H, m, ArH), 3.44 (2 H, d, CH_2OH), 2.72 (4 H, m, CH_2CHCH_2), 2.4—2.0 (1 H, m, $CH{\cdot}CH_2OH$), and 1.51 (1 H, s, exchanges with D_2O, OH) (Found: C, 73.2; H, 6.0%; M^+, 262. $C_{16}H_{16}F_2O$ requires C, 73.3; H, 6.15%; *M*, 262). The following alcohols and diols were prepared in a similar manner (and in the yields indicated) from the corresponding carboxylic acid and diethyl ester respectively.

3-(2-*Fluoro*-5-*methoxyphenyl*)*propanol* (**13**) (84%), b.p. 118—130 °C/1.1 mmHg; $\nu_{max.}$ 3 480 cm^{-1}; δ 7.0—6.4 (3 H, m, ArH), 3.66 (3 H, s, CH_3), 3.59 (2 H, t, CH_2OH), 2.62 (2 H, t, $ArCH_2$), 2.13 (1 H, s, exchanges with D_2O, OH), and 1.78 (2 H, m, CH_2CH_2OH) (Found: C, 64.9; H, 7.1; M^+, 184. $C_{10}H_{13}FO_2$ requires C, 65.2; H, 7.11%; *M*, 184).

2-(2-*Fluorophenylmethyl*)-2 (2-*fluoro*-5-*methoxyphenylmethyl*)*ethanol* (**14**) (83%), b.p. 144—152 °C/0.15 mmHg; $\nu_{max.}$ 3 420 cm^{-1}; δ 7.2—6.35 (7 H, m, 2 × ArH), 3.67 (3 H, s, CH_3), 3.4 (2 H, d, CH_2OH), 2.65 (4 H, d, 2 × $ArCH_2$), 2.4—1.8 (1 H, m, $CHCH_2OH$), and 1.7 (1 H, s, exchanges with D_2O, OH) (Found: C, 69.7; H, 6.3%; M^+, 292. $C_{17}H_{18}F_2O_2$ requires C, 69.85; H, 6.2%; *M*, 292).

2-(2-*Fluorophenylmethyl*)*propane*-1,3-*diol* (**8c**) (42%), b.p. 108—114 °C/0.1 mmHg; $\nu_{max.}$ 3 475 cm^{-1}; δ 7.4—6.83 (4 H, m, ArH), 3.87—3.48 (4 H, m, 2 × CH_2OH), 2.62 (2 H, d, $ArCH_2$), 2.32 (2 H, s, exchanges with D_2O, 2 × OH), and 2.25—1.85 (1 H, m, $ArCH_2CH$); $(M - 18)^+$, 166. $C_{10}H_{11}FO$ requires *m/z* 166.

2,2-*Bis*(2-*fluorophenylmethyl*)*propane*-1,3-*diol* (**10**) (72%), m.p. 77—80 °C (from chloroform–light petroleum); $\nu_{max.}$ 3 475 cm^{-1}; δ 7.5—6.8 (8 H, m, ArH), 3.44 (4 H, d, 2 × CH_2OH), 2.8 (4 H, s, 2 × $ArCH_2$), and 2.20 (2 H, s, exchanges with D_2O, 2 × OH) (Found: C, 70.0; H, 6.3; M^+, 292. $C_{17}H_{18}F_2O_2$ requires C, 69.85; H, 6.2%; *M*, 292).

4-(2-*Fluorophenyl*)*butan*-2-*ol* (**8b**).—4-(2-Fluorophenyl)-butan-2-one (**24**) was prepared in 66% yield by treatment of pentane-2,4-dione with 2-fluorobenzyl bromide and potassium carbonate in ethanol as described for the *meta* isomer.[16] The ketone had b.p. 113—117 °C/16 mmHg and showed $\nu_{max.}$ 1 710 cm^{-1}; δ 7.08 (4 H, m, ArH), 3.05—2.55 (4 H, m, CH_2CH_2), and 2.08 (3 H, s, CH_3). Addition of this ketone (3.4 g) in dry ether (20 ml) to lithium aluminium hydride (0.3 g) in dry ether (10 ml) afforded the *alcohol* (2.9 g, 84%), b.p. 110—116 °C/18 mmHg; $\nu_{max.}$ 3 450 cm^{-1}; δ 7.07 (4 H, m, ArH), 3.77 (1 H, m, CHOH), 2.72 (2 H, t, $ArCH_2$), 1.81 (1 H, s, exchange with D_2O, OH), 1.71 (2 H, q, CH_2CHOH), and 1.18 (3 H, d, CH_3) (Found: C, 71.45; H, 7.7%; M^+, 154. $C_{10}H_{13}FO$ requires C, 71.4; H, 7.8%; *M*, 168).

Ethyl (E)-3-(2-*Fluoro*-5-*nitrophenyl*)*prop*-2-*enoate*.—A suspension of 2-fluoro-5-nitrobenzaldehyde (10 g) in ethanol (50 ml) was added with stirring to (ethoxycarbonylmethylene)-triphenylphosphorane[17] (23 g) in ethanol (170 ml). The mixture was heated under reflux for 1 h, concentrated to a volume of *ca.* 100 ml, and then cooled and filtered to give the *ester* (7.6 g, 54%), m.p. 97—98 °C (from ethanol); $\nu_{max.}$ 1 640 and 1 720 cm^{-1}; δ 8.48 (1 H, m), 8.25 (1 H, m), and 7.27 (1 H, t) (ArH), 7.81 (1 H, d, *J* 16 Hz, ArCH=), 6.65 (1 H, d, *J* 16 Hz, COCH=), 4.30 (2 H, q, OCH_2), and 1.33 (3 H, t, CH_3) (Found: C, 55.1; H, 4.2; N, 5.6%; M^+, 239. $C_{11}H_{10}FNO_4$ requires C, 55.2; H, 4.2; N, 5.9%; *M*, 239).

3-(2-*Fluoro*-5-*nitrophenyl*)*propanol* (**12**).—A mixture of the preceding ester (4 g), tris(triphenylphosphine)chlororhodium(I) (0.5 g), and ethanol (250 ml) was shaken under dihydrogen until the calculated volume of the gas had been consumed. The mixture was filtered through Kieselguhr and the solvent was removed from the filtrate under reduced pressure to leave ethyl 3-(2-fluoro-5-nitrophenyl)propionate (3.9 g), $\nu_{max.}$ 1 740 cm^{-1}; δ 8.3—8.00 (2 H, m) and 7.17 (1 H, t) (ArH), 4.13 (2 H, q, OCH_2), 3.06 (2 H, t, $ArCH_2$), 2.67 (2 H, t, CH_2CO), and 1.21 (3 H, t, CH_3).

A solution of this ester (2 g) in dry tetrahydrofuran (30 ml) was added dropwise with stirring to lithium borohydride (300 mg) in the same solvent (30 ml) at 0 °C. The mixture was then heated under reflux for 1 h, cooled, and then diluted successively with water (10 ml), M-hydrochloric acid (20 ml), and water (50 ml). The organic material was extracted with ether (4 × 50 ml) and chromatographed on an alumina column using ethyl acetate in light petroleum as the eluant. This procedure afforded an oil (940 mg) which appeared to be a mixture of the desired alcohol and its acetate ($\nu_{max.}$ 1 745 cm^{-1}; δ 2.02, no signal at δ 2.67), the latter compound having been formed during the chromatography. This oil and toluene-*p*-sulphonic acid (2 g) were heated for 3 h in methanol (50 ml) under reflux, and then the mixture was poured into an excess of water. The organic material was extracted with ether to give the *alcohol* (830 mg, 50%), $\nu_{max.}$ 3 450 cm^{-1}; δ 8.3—8.0 (2 H, m) and 7.12 (1 H, t) (ArH), 3.68 (2 H, t, CH_2OH), 2.82 (2 H, t, $ArCH_2$), 2.08—1.68 (2 H, m, $CH_2{\cdot}CH_2OH$), and 1.74 (1 H, s, exchange with D_2O, OH) (Found: C, 54.3; H, 5.0; N, 7.0%; M^+, 199. $C_9H_{10}FNO_3$ requires C, 54.3; H, 5.1; N, 7.0%; *M*, 199).

2-(2-*Fluorophenyl*)*ethanol*.—Ethyl 2-(fluorophenyl)acetate[18] (6.5 g) in dry ether (30 ml) was added dropwise with stirring to lithium aluminium hydride (0.7 g) in dry ether (40 ml). The mixture was refluxed for 1 h, cooled, and treated with water (50 ml) and then with 2M-hydrochloric acid (50 ml). The organic material was extracted with ether and fractionated to give the *alcohol* (4.4 g, 88%), b.p. 104—106 °C/14 mmHg; $\nu_{max.}$ 3 400 cm^{-1}; δ 7.11 (4 H, m, ArH), 3.83 (2 H, t, CH_2OH), 2.89 (2 H, t, $ArCH_2$), and 1.68 (1 H, s, exchange with D_2O, OH) (Found: C, 68.6; H, 6.3. C_8H_9FO requires C, 68.5; H, 6.5%).

2-(2-*Fluorophenyl*)*ethyl Bromide*.—A mixture of the preceding alcohol (4.4 g), hydrobromic acid [48% (w/w), 6.6 g], and concentrated sulphuric acid (2.2 g) was heated under reflux for 6 h and then cooled and poured into water (50 ml). The organic material was extracted into ether and the extract was washed with saturated aqueous sodium hydrogen carbonate, dried, and fractionated to give the bromide (4.8 g, 75%), b.p. 73—75 °C/20 mmHg; δ 7.11 (4 H, m, ArH), 3.52 (2 H, t, CH_2Br), and 3.17 (2 H, t, $ArCH_2$); M^+, 203, C_8H_8BrF requires *M*, 203.

1-(2-*Fluorophenyl*)-3-*methyloctan*-3-ol (**19**).—Heptan-2-one (2.6 g) in ether (5 ml) was added dropwise with stirring to the Grignard reagent prepared from the preceding bromide (4.7 g) and magnesium (0.56 g) in ether (20 ml). The mixture was heated under reflux for 2 h and then cooled, and the organic material was isolated in the usual manner. Fractionation afforded the *tertiary alcohol* (2.8 g, 50%), b.p. 102—104 °C/0.1

mmHg; $\nu_{max.}$ 3 350 cm^{-1}; δ 7.08 (4 H, m, ArH), 2.91—2.51 (2 H, m, $ArCH_2$), 1.92—1.10 [14 H (13 H with D_2O shake), $CH_2C(CH_3)(OH)(CH_2)_4$], and 0.89 [3 H, t, $(CH_2)_4CH_3$] (Found: C, 75.5; H. 9.7. $C_{15}H_{23}FO$ requires C, 75.6; H, 9.7%); *m/z* 231 ($M - 17^+$. $C_{15}H_{22}F$ requires 231).

3-*Benzyloxy*-1-(2-*fluorophenyl*)*propanol* (**20**).—Ethyl 3-(2-fluorophenyl)-3-hydroxypropionate[19] (27 g) in ether (100 ml) was added dropwise with stirring to lithium aluminium hydride (4 g) in ether (50 ml) and the mixture was refluxed for 2 h and then cooled and processed in the usual manner to give 1-(2-*fluorophenyl*)*propane*-1,3-*diol* (13.2, 61%), m.p. 44—46 °C (from light petroleum–ethyl acetate); $\nu_{max.}$ 3 550 cm^{-1}; δ 7.62—6.84 (4 H, m, ArH), 5.22 (1 H, t, C*H*OH), 3.80 (2 H, t, CH_2OH), 3.57 and 2.91 [both 1 H and s, and exchange with D_2O; 2 × OH), and 1.93 (2 H, q, CH_2CH_2OH)] (Found: C, 63.5; H, 6.4%; M^+, 170. $C_9H_{11}FO_2$ requires C, 63.5; H, 6.5%; *M*, 170).

A mixture of this diol (12.5 g), benzyl bromide (21.5 g), sodium hydroxide (5 g), trioctyl(methyl)ammonium chloride (6 g), dichloromethane (1.2 l), and water (105 ml) was stirred vigorously under reflux for 15 days and then cooled. The organic layer was separated and dried, and the solvent was removed under reduced pressure to leave an oil which was chromatographed on a column of alumina (using ethyl acetate–light petroleum as the eluant) and then fractionated to give the *monobenzyl ether* (10.9 g, 57%), b.p. 134—136 °C/1 mmHg; $\nu_{max.}$ 3 575 cm^{-1}; δ 7.68—6.83 (m) and 7.31 (s) (ArH, total 9 H), 5.22 (1 H, t, ArC*H*OH), 4.49 (2 H, s, CH_2Ph), 3.66 (2 H, t, CH_2CH_2O), 3.12 (1 H, s, exchange with D_2O, OH), and 2.03 (2 H, q, CH_2CH_2OH) (Found: C, 73.8; H, 6.5%; M^+, 260. $C_{16}H_{17}FO_2$ requires C, 73.8; H, 6.6%; *M*, 260).

3-*Acetoxy*-3-(2-*fluorophenyl*)*propanol* (**22**).—A mixture of the preceding monobenzyl ether (5.1 g), acetyl chloride (1.65 g), and dry benzene (10 ml) was heated under reflux for 5 h and then cooled and poured into water (50 ml). The organic layer was separated, washed with saturated aqueous sodium hydrogen carbonate, dried, and fractionated to give 1-*acetoxy*-1-(2-*fluorophenyl*)-3-*benzyloxypropane* (**21**) (5.1 g, 86%), b.p. 136—139 °C/2 mmHg; $\nu_{max.}$ 1 740 cm^{-1}; δ 7.8—6.72 (m) and 7.28 (s) (ArH, total 9 H), 6.18 (1 H, t, ArC*H*OAc), 4.43 (2 H, s, CH_2Ph), 3.48 (2H, t, CH_2CH_2), 2.4—1.96 (m) and 1.97 (s) (CH_2CH_2O and CH_3 respectively, total 5 H) (Found: C, 71.5; H, 6.45%; M^+, 302. $C_{18}H_{19}FO_3$ requires C, 71.5; H, 6.3%; *M*, 302).

A mixture of this ester (4.9 g), palladium on charcoal (10%, 110 mg), and ethanol (50 ml) was shaken under dihydrogen until the calculated volume of the gas had been consumed. The mixture was filtered through Kieselguhr and the filtrate was fractionated to give the *alcohol* (3.2 g, 93%), b.p. 123—125 °C/1.3 mmHg; $\nu_{max.}$ 3 525 and 1 740 cm^{-1}; δ 7.6—6.85 (4 H, m, ArH), 6.21 (1 H, t, ArC*H*OAc), 3.63 (2 H, t, CH_2OH), and 2.36—1.68 (m) and 2.05 (s) (CH_2CH_2OH and CH_3 respectively, total 6 H, 5 H after D_2O shake) (Found: C, 62.2; H, 6.4%; M^+, 212. $C_{11}H_{13}FO_3$ requires C, 62.3; H, 6.2%; *M*, 212).

3-(2-*Fluorophenyl*)*propylamine* (**29**).—A mixture of 2-fluorobenzaldehyde (10.4 g), cyanomethyl(triphenyl)phosphorane[20] (26 g), and dry benzene (150 ml) was heated under reflux for 36 h after which the benzene was removed under reduced pressure. Ether (150 ml) was added to the residue and the resultant precipitate (Ph_3PO) was filtered off. Fractionation of the filtrate gave a mixture of the (*E*) and (*Z*) isomers of 3-cyano-1-(2-fluorophenyl)prop-1-ene (6.7 g, 90% based on recovered 2-fluorobenzaldehyde), b.p. 130—164 °C/23 mmHg; $\nu_{max.}$ 1 580, 1 613, 1 622, and 2 220 cm^{-1}; δ 7.43—6.70 (5 H, ArH and ArC*H*=), and 5.86 (d, *J* 16 Hz), and 5.38 (d, *J* 12 Hz), due to the (*Z*) and (*E*) forms of CH=C*H*CN respectively (total 1 H).

This unsaturated nitrile (7.3 g) in dry ether (30 ml) was added dropwise with stirring to lithium aluminium hydride (6 g) in ether (100 ml) and the mixture was heated under reflux for 45 min. The organic material was isolated in the usual manner and fractionated to give the primary amine (2.9 g, 38%), b.p. 108—109 °C/12 mmHg; $\nu_{max.}$ 3 250 cm^{-1}; δ 6.94 (4 H, m, ArH), 2.62 (4 H, $ArCH_2$ and CH_2NH_2), 1.77 (2 H, s, exchange with D_2O, NH_2), and 1.66 (2 H, m, $CH_2CH_2NH_2$).

N-*Ethyl*-3-(2-*fluorophenyl*)*propylamine* (**30**).—A mixture of the preceding amine (1 g), hydrated sodium acetate (1.7 g), acetaldehyde (3.5 ml), acetic acid (5.4 ml), ethanol (13 ml), and water (16 ml) was stirred at 0 °C for 10 min and then sodium borohydride (1.3 g) was added portionwise over 30 min. The mixture was basified with 10% (w/v) aqueous potassium hydroxide and the organic material was extracted with ether and fractionated to give the secondary amine (0.33 g, 28%), b.p. 114—124 °C/22 mmHg; $\nu_{max.}$ 3 380 cm^{-1}; δ 7.06 (4 H, m, ArH), 2.51 (6 H, $ArCH_2$ and CH_2NHCH_2), 2.05 (1 H, s, NH), 1.65 (2 H, m, CH_2CH_2NH), and 1.0 (3 H, t, CH_3).

3-(2-*Fluorophenyl*)*propanamide* (**26**).—A mixture of 3-(2-fluorophenyl)propanoic acid (6.8 g) and thionyl chloride (5.9 ml) was heated under reflux for 1 h and then fractionated to give 3-(2-fluorophenyl)propionyl chloride (6.1 g, 81%), b.p. 128—134 °C/23 mmHg (lit.,[21] b.p. 82—83 °C/2 mmHg); $\nu_{max.}$ 1 800 cm^{-1}. This acid chloride (1.2 g) was added dropwise to an aqueous solution of ammonia [30% (w/w), 3 ml] and the mixture was stirred for 18 h and then filtered to give the *primary amide* (0.9 g, 84%), m.p. 100—101 °C (from aqueous ethanol; $\nu_{max.}$ 1 630, 1 650, 3 275, and 3 450 cm^{-1}; δ 7.1 (4 H, m, ArH), 5.65 (2 H, s, exchanges with D_2O, NH_2), 2.98 (2 H, t, $ArCH_2$), and 2.48 (2 H, t, CH_2CO) (Found: C, 64.5; H, 6.0; N, 8.2%; M^+, 167. $C_9H_{10}FNO$ requires C, 64.7; H, 6.0; N, 8.4%; *M*, 167).

3-(2-*Fluorophenyl*)-N-(*t-butyl*)*propanamide* (**27**) was prepared similarly (70% yield) from the acid chloride (1.2 g) and t-butylamine (3.9 g) in water (7.3 ml). This *secondary amide* had m.p. 90—91 °C (from aqueous ethanol), $\nu_{max.}$ 1 640, 1 655, and 3 375 cm^{-1}; δ 7.09 (4 H, m, ArH), 5.1 (1 H, s, NH), 2.96 (2 H, t, $ArCH_2$), 2.36 (2 H, t, CH_2CO), and 1.27 (9 H, s, 3 × CH_3) (Found: C, 69.8; H, 8.1; N, 6.1%; M^+, 223. $C_{13}H_{18}FNO$ requires C, 69.9; H, 8.1; N, 6.3%; *M*, 223).

3-(2-*Fluorophenyl*)*propanethioamide* (**28**).—A mixture of 3-(2-fluorophenyl)propanamide (0.5 g), 2,4-bis(4-methoxyphenyl)-1,3,2,4-dithiadiphosphetane 2,4-disulphide (Lawesson's reagent, 0.61 g), and hexamethylphosphoramide (5 ml) was heated at 80 °C for 4 h and then cooled and poured into water (10 ml). The organic material was extracted with ether and chromatographed on a column of alumina with ethyl acetate–light petroleum as the eluant to give the *thioamide* (0.35 g, 64%), m.p. 63—65 °C (from chloroform–light petroleum); $\nu_{max.}$ 1 620, 1 640, 3 200, and 3 425 cm^{-1}; $\lambda_{max.}$ 209, 264, and 269 (ε 9 970, 11 800, and 12 600 respectively); δ 7.86—6.25 and 7.12 (m) (NH_2 and ArH respectively, total 6 H), and 3.4—2.8 (4 H, CH_2CH_2) (Found: C, 58.9; H, 5.6; N, 7.9%; M^+, 183. $C_9H_{10}FNS$ requires C, 59.0; H, 5.5; N, 7.6%; *M*, 183).

Rhodium-catalysed Cyclisation of the Fluoro Alcohol (**13**).—A mixture of the fluoro alcohol (0.54 g), the salt (**3**) (0.30 g), acetone (1.7 ml), and nitromethane (8.7 ml) was heated at 80 °C under dinitrogen for 4 days, and then dimethyl sulphoxide (6 ml) was added and the heating was continued for 1 h. The mixture was cooled and diluted with water (50 ml), and the organic material was extracted with ether and chromatographed on a column of alumina with light petroleum as the eluant to give 6-methoxychroman (0.17 g); δ 6.8—6.5 (3 H, m, ArH), 4.11 (2 H, t, CH_2O), 3.61 (3 H, s, CH_3), 2.74 (2 H, t, $ArCH_2$), and 1.94 (2 H, m, CH_2CH_2O) (Found: C, 73.3; H, 7.4%; M^+, 164. Calc.

for $C_{10}H_{12}O_2$: C, 73.1; H, 7.4%; *M*, 164). Further elution of the column with 30% (v/v) ethyl acetate in light petroleum afforded unchanged fluoro alcohol (0.15 g).

The following chromans were prepared in a similar manner from the corresponding fluoro alcohols (yields given in Table).

2-Methylchroman (**9b**); δ 7.25—6.65 (4 H, m, ArH), 4.3—3.9 (1 H, m, C*H*CH_3), 2.9—2.66 (2 H, m, $ArCH_2$), 2.1—1.45 (2 H, m, $ArCH_2CH_2$), and 1.34 (3 H, d, CH_3) (Found: C, 80.9; H, 8.0%; M^+, 148. Calc. for $C_{10}H_{12}O$: C, 81.0; H, 8.2%; *M*, 148).

3-*Hydroxymethylchroman* (**9c**) as an oil; δ 7.25—6.7 (4 H, m, ArH), 4.44—3.82 (2 H, m, $ArOCH_2$), 3.62 (2 H, d, CH_2OH), 3.04—2.52 (2 H, m, $ArCH_2$), 2.52—2.1 (1 H, m, C*H*CH_2OH), and 2.02 (1 H, s, exchanges with D_2O, OH) (Found: C, 73.15; H, 7.4%; M^+, 164. $C_{10}H_{12}O_2$ requires C, 73.15; H, 7.4%; *M*, 164).

3-(2-*Fluorophenylmethyl*)*chroman* (**9d**), m.p. 53—54 °C; δ 7.4—6.7 (8 H, m, ArH), 4.27—3.68 (2 H, m, OCH_2), 3.0—2.5 (m, 4 H, 2 × $ArCH_2$), and 2.5—2.18 (1 H, m, C*H*CH_2O) (Found: C, 79.2; H, 6.2%; M^+, 242. $C_{16}H_{15}FO$ requires C, 79.3; H, 6.2%; *M*, 242).

3,3′-*Spirobichroman* (**11**), m.p. 114—115 °C (from light petroleum); δ 7.3—6.7 (8 H, m, ArH), 2.67 (4 H, ABq, $ArCH_2$), and 3.94 (4 H, s, CH_2O) (Found: C, 80.85; H, 6.6%; M^+, 252. $C_{17}H_{16}O_2$ requires C, 80.9; H, 6.4%; *M*, 252).

Reaction of the Fluoro Alcohol (**22**) *with the Salt* (**3**).—A mixture of the fluoro alcohol (36 mg), the salt (17 mg), acetone (0.1 ml), and [$^2H_3$]nitromethane (0.5 ml) was heated at 80 °C for 24 h, and then dimethyl sulphoxide (0.3 ml) was added and the heating was continued for a further 1 h. The mixture was cooled and poured into water (20 ml), and the organic material was extracted with ether to give an oil (29 mg); $\nu_{max.}$ 1 730 cm^{-1}; δ 7.67—6.65 (5 H, ArH and ArCH=), 4.96—4.42 (1 H, m, CH_2CH=), 4.41—3.92 (2 H, m, CH_2O), and 1.99 (3 H, s, CH_3); *m*/*z* (chemical ionisation with CH_4) 195, 135, and 109.

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