Double-bond Migration in Pyrano[4,3-*b*]pyrylium Cations

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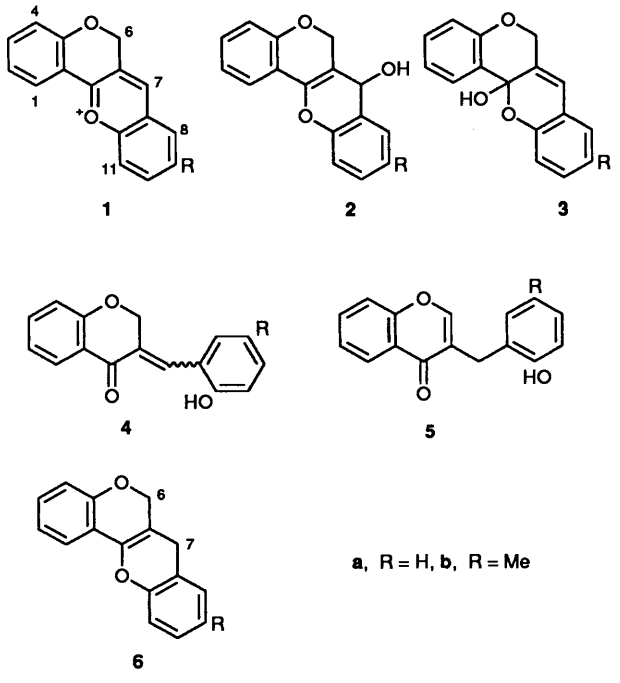
That hydrolysis of [1]benzopyrano[4,3-*b*][1]benzopyrylium derivatives **1** includes a double-bond shift giving derivatives **5** of 3-(2-hydroxybenzyl)[1]benzopyran-4-ones has been confirmed. Chromones like **5** are related to the 7*H*-[1]benzopyrano[3,2-*c*][1]benzopyrylium cations **9** into which they are transformed by strong acids. The double bond shift occurs in the cations and is mediated not by prototropy but by hydride exchanges *via* the 6*H*,7*H*-[1]benzopyrano[4,3-*b*][1]benzopyrans **6**, thus: **1** + **6** ⇌ **6** + **1** and **1** + **6** ⇌ **6** + **9**. The equilibria favour the cations **9** which are hydrolysed by water to the chromones **5**. Initiation occurs when the cations **1** add water giving the alcohols **2** which reduce them to the catalysts **6** and are themselves oxidised to 6*H*,7*H*-[1]benzopyrano[4,3-*b*][1]benzopyran-7-ones **7**.

In perchloric acid, chromanone (2,3-dihydro-[1]benzopyran-4-one) condenses with 2-hydroxybenzaldehyde to give the expected 1-benzopyrylium cation[1] **1a**. This cation should, in theory, react with water and base to form the alcohols **2a** and **3a** and from the latter the phenolic chalcone **4a**. Surprisingly, however, the only product identified was the isomeric phenol **5a** with a chromone nucleus.[1,2] This migration of a double bond closely parallels one required in a route to fulvic acid[3] where, in contrast, it is difficult to achieve, and we have, therefore, repeated and extended the previous study to uncover the mechanism.

We prepared **1a** as the perchlorate as described by previous workers, but obtained a satisfactorily pure product only by omitting the recommended recrystallisation from acetic acid. The homologous cation **1b** was prepared similarly. Addition of the perchlorates to aqueous sodium acetate supplied the phenolic chromones **5a** and **5b**, the structures of which were



confirmed by the ^{1}H NMR spectroscopy (Table 1) and by the mass spectrum of the former. The chief peaks in this suggested substantial ring closure with loss of OH to regenerate ion **1a** or an isomer, along with simple fragmentations breaking the links on either side of the CH_2 group in the molecular ion.

We confirmed that borohydride ion in tetrahydrofuran reduces the cation **1a** to the pyranopyran **6a** by adding hydride ion to the 4-position of the pyrylium ring in the expected way,[4] and agree that borohydride in ethanol leads not to reduction but to a complex mixture from which a poor yield of the phenolic chromone **5a** can be obtained.[2] The homologue **1b** behaved in the same way, and an NMR study showed the formation of several products (not isolated) containing ethoxy groups; evidently, in ethanol the borohydride reacts as a base only, inducing a variety of reactions (including dimerisations) similar to those described by Reynolds and van Allan for simpler pyrylium salts.[5]

The double-bond shift is not base-catalysed. In the cation **1a** removal of a proton from the 6-methylene group would leave a system with no way of using the oxonium centre to stabilise the anionic charge; and no shift would be expected in the related chalcone **4a** as this still lacks activation for the methylene group. Barton, Magnus and Okogun[6] succeeded in effecting such a shift in a similar chalcone but even though a weakly activating group was present the reaction required triethylamine at over 140 °C for 5 h. Furthermore, we found that bases are unnecessary; the reaction occurs at a moderate pace in warm acetic acid, which accounts for our inability to purify the salt using this solvent and provides the best preparative method for the chromone.

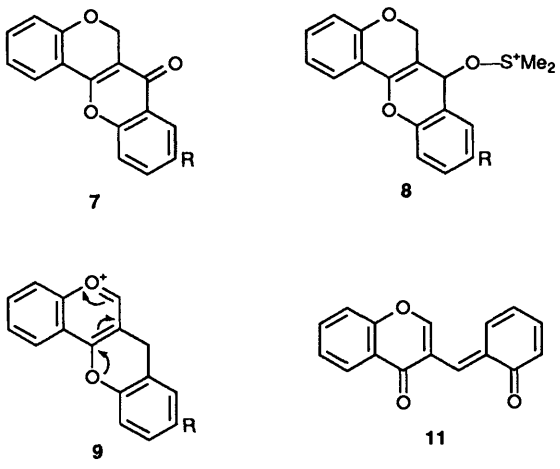
When the perchlorate of **1a** is kept in damp acetonitrile, the phenolic chromone **5a** crystallises during several days. The yield is very good (89%) but the mixture remains dark red and also yields a small amount (1.2%) of the pyranopyrone **7a**, which is formally an oxidation product of the initial alcohol **2a**. These conditions permitted us to monitor the reaction by ^{1}H NMR spectroscopy and to establish that the salt does not change in dry acetonitrile until water is added whereafter it reacts smoothly giving the phenolic chromone. Deuterium oxide gives the same product as water, no deuterium becoming attached to carbon and thus confirming the absence of prototropy. The reaction is largely complete in a few hours, the extra time (days) being needed only for the chromone to crystallise. The spectra afford little evidence for the presence of any other products except for a weak AB quartet (δ_A 4.22, β_B 4.39; J_{AB} 12.6 Hz) not observed until the salt had been almost entirely consumed and which might correspond to the alcohol **3a**, other signals being overlaid. The red colour persisting to the end might be attributed to traces of the chalcone **4a**.

A related reaction was observed by dissolving the salt **1a** in dimethyl sulfoxide; the colour lightened immediately suggesting

Table 1 ^{1}H NMR spectra[a] (δ scale)

Compound	Structure number	Benzenoid protons 1	2	3	4	8	9	10	11	OCH= 6	OCH_2 6	ArCH= 7	$ArCH_2$ 7	Me	Conditions
Cation (perchlorate)	**1a**	8.22 d, 7.6	7.31 t, 7.8	7.86 m	7.20 d, 8.6	8.25 d, 7.1	7.92 t, 8.1	8.17 t, 8.4	8.25 d, 7.1		5.76 s	9.03 s			*b*
Cation (perchlorate)	**1a**	8.46 dd, 8.1, 1.8	7.45 td, 7.3, 1	8.02 m	7.34 br d, 8.6	8.37 d, 7?	8.07 m	8.37 d, 8.3	8.37 s		5.72 s	9.04 s			*c*
Cation (perchlorate)	**9a**	8.64 dd, 7.8, 1.5?	8.05 t, 7.8	8.34 t, 7.6	8.16 d, 6.8	7.46 d, 7.4	7.43 t?	7.43 t?	7.46 d, 7.4	9.35 s			4.48 s		*b*
Cation (perchlorate)	**1b**	8.35 dd, 8, 2	7.43 t	7.94 t	7.30 d, 8	8.06 s		8.17 s	8.17 s		5.80 s	9.00 s		2.70 s	*d*
Cation (perchlorate)	**9b**	8.63 dd, 8, 2	8.04 t, 7	8.33 t, 7	8.17 dd, 8, 2	7.22 s		7.37 d, 8	7.28 d, 8	9.26 s			4.42 s	2.42 s	*b, d*
Pyranopyran	**6a**	7.52 dd, 7.4?	6.96 t, 8.1	7.16 t, 7.4	6.82 dd, 8.1, 1	*ca.* 7	6.96 t, 8.1	7.05 t, 7.4	7.05 d, 8.4		4.82 s		3.36 s		*e*
Pyranopyran	**6b**	7.52 dd, 7.5, 2	*ca.* 7	7.18 t	6.81 d, 8	6.8 s		*ca.* 7	6.83 d, 8		4.82 s		3.31 s	2.29 s	*f*
Dihydropyranopyran	**10**	7.65 d, 7.7	*ca.* 7 m	7.05 t, 8	6.88 dd, 8.3, 2.5	*ca.* 7 m		*ca.* 7 m	*ca.* 7 m		(6 spin multiplet system; see text)			2.28 s	*b*
Pyranopyrone	**7a**	7.82 dd, 7.7, 1.7	7.07 td, 7.6, 1.1	*ca.* 7.4 m	6.96 dt, 8.3, 1.1	8.22 dd, 7.9, 2.7	*ca.* 7.4 m	7.69 dt, 7.7, 1.7;	7.54 dd, 8.4, 1.2		5.38 s				*e*
Pyranopyrone	**7b**	7.47 dd, 8, 2	7.05 t, 8	7.37 t, 8	6.94 d, 8	7.97 d, 2		7.78 dd, 8, 2	7.41 d, 8		5.32 s			2.42 s	*f*
Chromone[g]	**5a**	8.15 dd, 8.0, 1.5	7.33 t, 7.6	7.67 td?, 8, 2	7.38 d, 7.7	*ca.* 7.09 d, *ca.* 8	6.79 t, 7.4	*ca.* 7.08 t *ca.* 8	6.92 d, 8.5	8.04 s			3.70 s	(9.22)[h]	*f*
Chromone[g]	**5b**	8.22 dd, 7.5, 2	7.39 td, 7.5, 1	7.67 td, 8, 2	7.44 dd, 8, 1	6.92 br s		6.93 br d	6.86 d, 8.5	8.09 s			3.69 s	2.22 s	*f*

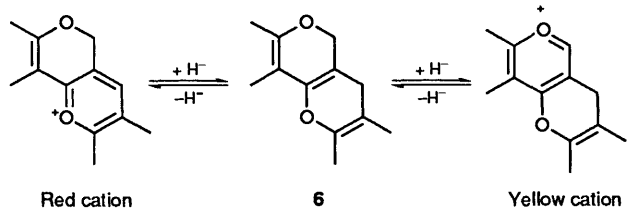
[a] Relative intensities are those required by the assignments. Multiplicities and first order splittings (Hz) are shown below the corresponding chemical shifts. Details for previously known compounds confirm and extend earlier reports. [b] $CDCl_3/F_3CCO_2H$ 9:1; FT 200 MHz. [c] CD_3CN; FT 250 MHz; double irradiation experiments confirmed couplings between 4-H and 3-H, 2-H and 3-H, and 2-H and 1-H. [d] $CDCl_3/F_3CCO_2H$, 9:1; CW 220 MHz. [e] $CDCl_3$; FT 200 MHz. [f] $CDCl_3$; CW 220 MHz. [g] For the purposes of this Table only, numbering is taken from the benzopyranobenzopyran system. [h] Removed by D_2O; OH.



the formation of the adduct **8**, the ^{1}H NMR spectrum showing this to be the major product although we failed to isolate it. Since all the aromatic protons resonate at fields above δ 7.9, oxonium and carbonyl groups are absent. An AB quartet (δ_A 4.87, δ_B 4.81, J_{AB} 13 Hz) signals the CH_2O group while a singlet at 5.12 signals the methine proton in the $ArCHOSMe_2$ group. Moreover, after adding pyridine we obtained a variable (not less than 30%) yield of the condensed pyrone **7a**.

The isomerisation is not acid catalysed. The cations (**1a**; **1b**) are stable indefinitely in trifluoroacetic acid, or in aqueous solvents containing perchloric acid, even when heated, and they can be purified by crystallisation from acetic acid containing one of these stronger acids. Conversely, perchloric acid converts the phenolic chromones **5a**, **b** into the respective yellow cations **9a**, **b**, the NMR spectra (Table 1) of which clearly distinguish them from the corresponding red cations **1a**, **b** thus removing any residual doubt about the constitution of the original red salts. Since upon treatment with water the yellow salts at once collapse giving the phenolic chromones **5a**; **5b** to which they are directly related they could be intermediates in their formation.

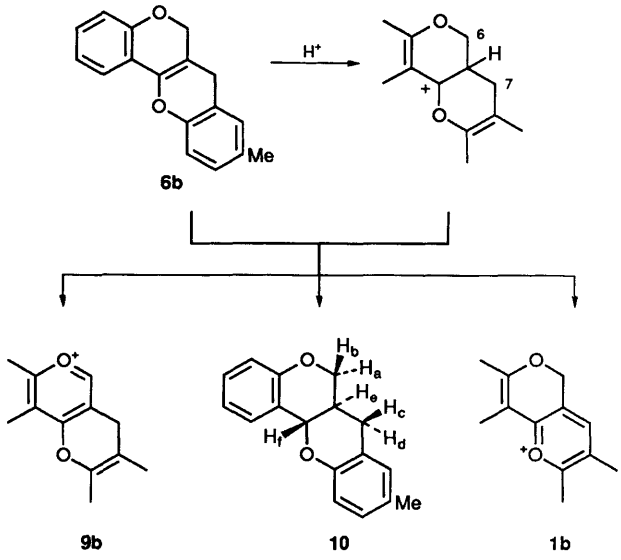
Direct evidence supports oxidation–reduction as the basis of the double-bond shift. We examined the idea that a red salt can add hydride at position 7 giving a pyranopyran **6** which might then lose hydride ion from position 6 to give a yellow salt (Scheme 1). Once started, such a system could cycle to



Scheme 1 Interconversion of red and yellow cations *via* hydride shifts

equilibrium; water being available, the yellow salt would be continuously lost as phenolic chromone until completion of the reaction.

Triphenylpyrylium perchlorate readily removes hydride from benzopyrans.[7] It oxidised pyranopyran **6a** instantly but only at position 7 to precipitate the red salt **1a** as reported by previous workers.[2] From a different reaction, however, we obtained clear evidence for loss of hydride from position 6. Thus, when the pyranopyran **6b** was treated in trichloromethane with trifluoroacetic acid to induce the dismutation characteristic of chromenes[8] the ^{1}H NMR spectra showed an immediate, clean reaction producing the dihydropyranopyran **10** (which we consider to be *trans*-fused as explained in the Experimental section) together with both the red salt **1b** and the yellow salt **9b** (Scheme 2). After the initial reaction there was no change in



Scheme 2 Dismutation of pyranopyran **6b** in trifluoroacetic acid

the ratio 2:1 of red to yellow cation. Presumably, the dihydropyranopyran is too poor a hydride donor to act as the required cycling catalyst; it seems improbable that equilibrium had already been attained because the yellow cation should be the more stable on account of the ability of the two oxygen atoms to share the charge (indicated by arrows in **9**) in a way not possible in the isomer.

The pyranopyrans **6** must be much better hydride donors because they attain aromaticity in the act. Accordingly, the interchange between the cation **1a** and the pyranopyran **6b** in deuteriated acetonitrile could be watched by means of the ^{1}H NMR spectra both as changes in the red salt/yellow salt ratio and as the methyl substituent (originally confined to the pyranopyran) gradually became distributed amongst the salts. At one stage or another the system contains at least 11 known components and so the estimates are probably not very accurate but, by means of one resonance or another, the main events can be followed (Table 2). A few minutes after the start the mixture contains not only the red cation **1a** but also substantial amounts of the homologue **1b** showing that the initial hydride transfer is under way but is not yet complete. Only traces of yellow salts can be seen; there has been no time yet for appreciable cycling. During the next few hours the two red salts diminish while cycling produces increasing amounts of the two yellow cations **9a**, **b** until only these are seen. This imbalance is consonant with the relative thermodynamic stability of the yellow salts mentioned above. During the later stages the two phenolic chromones **5a**, **b** become important components, presumably because the yellow cations are partly hydrolysed by the water present. This would make the reaction mixture more acidic which would, in turn, begin to destroy by dismutation and other reactions the pyranopyran components. After 18 h no characteristic signals from these can be detected.

The origin of the pyranopyran catalyst **6** has to be identified. In contact with water, the red cations **1** will react reversibly giving carbinols including **2** even if equilibrium does not favour them (they were not detected). Pyrilium salts readily oxidise secondary or benzylic alcohols to carbonyl compounds,[2,9] so oxidation of **2** by **1** would provide the required pyranopyran **6** and also account for the presence of the pyranopyrone **7**. Thus, strongly acidic media stabilise the red salts in two ways:

Table 2 Interaction of the pyrylium salt **1a** with the pyranopyran **6b**[a]

Monitor frequency (Hz)	Normalised intensities[b] at stated times after initial mixing					Compound structure	Proton assignment
	5 min	1h	2 h	3 h	18 h		
1858	0.7	2.3	5.2	9.5	9.1	salt **9a**	ArCH=
1850	0.5	1.0	2.7	4.1	5.3	salt **9b**	ArCH=
1800	5.6	3.8	1.5			salt **1a**	O-CH=
1781	4.2	2.6	2.3	0.5		salt **1b**	O-CH=
1718[c]		2.6	6.5	15.5	13.8	salts **9a, b**	H-1
1141[d]	12.7	10.0	3.8	0.9		salt **1a**	O-CH_2
1135[d]	12.3	9.5	5.5	2.0		salt **1b**	O-CH_2
956.0[e]	15.0	16.9	15.8	7.0		pyrans **6a, b**	O-CH_2
866.6		3.1	10.8	20.7	16.1	salts **9a, b**	ArCH_2
741.0[f]				2.3	16.1	chromone **5a**	ArCH_2
731.5[f]					12.3	chromone **5b**	ArCH_2
661.0	7.8	7.4	7.1			pyrans **6a, b**	ArCH_2
519.5	16.8	14.8	9.4	2.7		salt **1b**	Me
474.1[f]	7.2	7.9	15.7	23.6	18.1	salt **9b**	Me
450.4[f]	17.0	16.9	13.7	11.3		pyran **6b**	Me
439.7[f]					9.3	chromone **5b**	Me

[a] Salt **1a** (15 mg, 0.045 mmol) and pyranopyran **6b** (11 mg, 0.045 mmol) in CD_3CN (2 cm^3) containing water (2.5 mm^3). [b] Estimated by peak heights only. [c] Overlapping doublets not assessed separately. [d] Doublet J 1.2 Hz. [e] Centre of m produced by long-range coupling. [f] Partially obscured by water band in some scans.

opposing the formation of the initiator alcohol and destroying by dismutation the cycling pyranopyran.

In the original reaction the solid red salt was treated with bases; it was relatively fast but gave low yields.[2] Such conditions and especially the extreme heterogeneity might require some modification of these proposals. For example, they might generate the phenolic chalcone **4** (or its anion) which would be very easily oxidised (by the cations) to a quinone methide **11** and then reduced again.[10] This would also lead to double bond migration, because hydride ion can be taken only from the methylene group but when returned can be added at the alternative site.

Experimental

Unless other specifications are made, the following conditions apply. M.p. determinations were made by hot-stage methods and are uncorrected. Product purity for compounds other than salts were checked by thin layer chromatography on Kieselgel 60 F_{254} plates; column chromatography was carried out on pre-activated silica gel 60, 40–63 μm, under nitrogen at 2 psi.

IR spectra were obtained on a PE 125 spectrophotometer using KBr discs and UV spectra on a Unicam SP800 instrument. Mass spectra were determined by means of a V.G. analytical 7070E spectrometer.

Light petroleum refers to the fraction b.p. 60–80 °C. When necessary, solvents were dried during 2 days over appropriate molecular sieves.

The 70% perchloric acid used was the commercial variety containing water.

Preparation and Isomerisation of 6H-[1]*Benzopyrano*[4,3-b][1]*benzopyrylium Perchlorate* **1a**.—Chroman-4-one (8.58 g) was condensed with 2-hydroxybenzaldehyde (8.57 g) in acetic acid (40 cm^3) at 10 °C by the addition of perchloric acid in acetic acid (prepared as for the methylbenzopyrylium salt above) (50 cm^3). After 20 min dry ether was added to the dark red solution and the mixture left for 1 h. The precipitate was collected, washed with ether and dried *in vacuo* to give a red powder (9.15 g, 47%), m.p. 234 °C (decomp.), λ_{max}($MeCO_2H$)/ nm 461, 374, 278 and 249, identified by ^1H NMR spectroscopy as the salt described by earlier authors.[1] Crystallisation of this salt could be effected from acetic acid if conducted rapidly, but only once. Further crystallisations destroyed the salt unless the acetic acid contained a little perchloric acid. The salt could be kept indefinitely at 58 °C in trifluoroacetic acid (dried by distillation with the anhydride) or in trifluoroacetic acid containing water (5% by volume), or in acetic acid at 58 °C containing 5% trifluoroacetic acid.

The salt (0.17 g, 0.72 mmol) was heated in acetic acid (commercial 'glacial'; 25 cm^3) until the red colour had changed to yellow (up to 3 h). Left to cool, the solution deposited 7H-[1]*benzopyrano*[3,2-c]*benzopyrylium perchlorate* **9a** as yellow flakes (0.09 mg, 55%), m.p. 207 °C (decomp.), λ_{max}(AcOH)/nm 372, 308 and 248 (Found: C, 56.5; H, 3.7. $C_{16}H_{11}ClO_6 \cdot \frac{1}{2}H_2O$ requires C, 56.2; H, 3.5%).

3-(2-*Hydroxybenzyl*)[1]*benzopyran-4-one* (**5a**).—The requisite benzopyrylium perchlorate **1a** (2.95 g, 8.81 mmol) in acetonitrile (120 cm^3) containing water (1.5 cm^3) gradually deposited large irregular brownish crystals. A further quantity of water was added to the solution which was then left for 2 days to give a further crop of the benzopyranone. A repetition gave a third crop containing heavy prisms mixed with slender needles; the latter product was separated by floating it away with a little chilled acetonitrile and then ether. A final crop of prisms was secured by removing the solvent from the mother liquor and subjecting the residue to chromatography on silica. Combined and purified from propan-2-ol, the combined batches of prisms gave the hydroxybenzylbenzopyranone as prisms (1.96 g, 89%), m.p. 179 °C; λ_{max}(AcOH)/nm 312 and 231, identical with a sample prepared according to earlier authors.[2] The needles differed from the prisms in being insoluble in cold alkali and separated from ethyl acetate containing ethanol to give 6H-[1]*benzopyran*[4,3-b]*benzopyran-7-one* **7a** as long, hexagonal prisms (36 mg, 1.6%), m.p. 174–175 °C (subl.): ν_{max}/cm^{-1} 1640 (C=O) (Found: M, 250.0633. $C_{16}H_{10}O_3$ requires M, 250.0630). The solution in methanol has a blue fluorescence and the bright yellow solution in sulfuric acid has a green fluorescence.

(ii) To the benzopyrylium salt **1a** (700 mg) in acetonitrile (20 cm^3) under nitrogen was added water (0.1 cm^3); the flask was sealed and left for several days. The dark red solution desposited the phenolic benzopyranone **5a** as wide plates (221 mg, 42%), m.p. 181–182 °C, without further purification. Use of [$^2H_2$]-water in an identical experiment gave crystals, m.p. 179–182 °C, with a mass spectrum (EI, solid probe) indicating

$C_{16}H_{11}DO_3$ (M + 1 ion 79% instead of normal 19%). After a solution of the product in dichloromethane had been washed with water (to replace OD by OH) and recovered (without recrystallisation) the mass spectrum indicated $C_{16}H_{12}O_3$; the NMR spectrum was identical with that of a non-deuteriated sample.

9-*Methyl*-6H-[1]*benzopyrano*[4,3-b][1]*benzopyrylium Perchlorate* **1b**.—Perchloric acid (70%; 200 g) was added dropwise to acetic anhydride (340 g) stirred at −11 °C. A portion of this solution (9.3 cm^3, 18 mmol of perchloric acid) was added in drops to a mixture of 2-hydroxy-5-methylbenzaldehyde (2.2 g, 16.2 mmol) and chroman-4-one (2.18 g, 14.7 mmol) stirred in acetic acid (15 cm^3) at 10 °C. After 5 min, the dark red solution was diluted with ether (150 cm^3) to give a red precipitate which was collected and rapidly crystallised from acetic acid containing one drop of perchloric acid. This afforded the *benzopyrylium perchlorate* as brilliantly red plates (4.52 g, 80%), m.p. 210 °C (decomp.), $\lambda_{max}(HClO_4)$/nm 455, 373, 283 and 265 (ε 747, 421, 349 and 410) (Found: C, 58.2; H, 3.8. $C_{17}H_{13}ClO_6$ requires 58.5; H, 3.8%).

9-*Methyl*-6H,7H-[1]*benzopyrano*[4,3-b][1]*benzopyran* **6b**.—Sodium borohydride (190 mg) in tetrahydrofuran (5 cm^3) was added to a vigorously stirred suspension of the benzopyrylium salt **1b** (1 g) in the same solvent (40 cm^3) at 0 °C. After 30 min, the mixture was poured into ice-cold water (50 cm^3) containing concentrated hydrochloric acid (2 cm^3) and extracted with ether (3 × 100 cm^3). The combined extracts were washed with water, dried (Na_2SO_4), and evaporated under reduced pressure. The residue crystallised from ethanol to give the *benzopyranobenzopyran* as needles (501 mg, 70%), m.p. 75 °C; λ_{max}(MeCN)/nm 339 and 323 (ε 131 and 197); ν_{max}/cm^{-1} 1695, 1600, 1585 and 1575 (Found: C, 81.5; H, 5.6%; M^+, 250.098 82. $C_{17}H_{14}O_2$ requires C, 81.6; H, 5.6%; M^+, 250.099 36).

3-(2-*Hydroxybenzyl*)-6-*methyl*[1]*benzopyran*-4-*one* **5b**.—(i) The benzopyrylium salt **1b** (1 g) in ethanol (50 cm^3) was treated with sodium borohydride (109 mg) also in ethanol (5 cm^3) for 20 min and then poured into ice-cold water (100 cm^3) containing concentrated hydrochloric acid (2 cm^3). The mixture was extracted with ether (3 × 50 cm^3), and the combined extracts were washed with brine and worked up to afford a dark green semi-solid oil. This was flash chromatographed on silica from toluene–ethyl acetate (9:1, v/v) to give the *benzopyranone* which separated from propan-2-ol as plates (80 mg, 31%), m.p. 182 °C; ν_{max}/cm^{-1} 3110br (OH), 1620 (C=O), 1590 and 1565 cm^{-1} (Found: C, 76.7; H, 5.3%; M^+, 266.094 29. $C_{17}H_{14}O_3$ requires C, 76.7; H, 5.3%; M^+, 266.094 28). Further elution gave evidence of at least six more substances, the ^1H NMR spectra of which indicated the presence of EtO groups in five of them; no further examination was, however, undertaken.

(ii) A solution of the benzopyrylium salt **1b** (700 mg) in warm acetic acid (10 cm^3) was diluted with water (3 cm^3) and the mixture left overnight. The benzopyran-4-one separated as plates (330 mg, 63%), m.p. 181–182 °C, identical with a sample from (i).

9-*Methyl*-7H-[1]*benzopyrano*[3,2-c][1]*benzopyrylium Perchlorate* **9b**.—To the benzopyranone **5b** (540 mg) in acetic acid (20 cm^3) containing ethyl acetate (5 cm^3) was added 70% perchloric acid (1 cm^3). The flask was flushed with nitrogen and after 16 h the product was precipitated by the addition of ether (100 cm^3) and crystallised from acetic acid to provide the *benzopyrylium perchlorate* as tiny orange needles (361 mg, 51%), m.p. 245 °C (decomp.); $\lambda_{max}(HClO_4)$/nm 378 and 308 (ε 196 and 245); ν_{max}/cm^{-1} 1625, 1610, 1600 and 1080br (ClO_4^-) [Found (on specimen dried *in vacuo* over P_2O_5 for 48 h): C, 57.0; H, 3.95. $C_{17}H_{13}ClO_5$ requires C, 58.54; H, 3.73%; $C_{17}H_{13}ClO_5 \cdot \frac{1}{2}H_2O$ requires C, 57.14; H, 3.96%].

Conducted as in the preceding experiment (ii), the reaction of this salt with water in acetonitrile instantly regenerated the phenolic benzopyranone which separated as prisms, m.p. 180–182 °C.

9-*Methyl*-6H-[1]*benzopyrano*[4,3-b][1]*benzopyran*-7-*one* **7b**.—The benzopyrylium perchlorate **1b** (1.4 g) in dimethyl sulfoxide (20 cm^3) at room temperature was treated with triethylamine (distilled from calcium oxide and stored over molecular sieve type 5A; 0.6 cm^3) which induced immediate decolorisation. The solution was poured into ice–water (100 cm^3) and extracted with ether (3 × 50 cm^3). The combined extracts were washed with brine and water, dried ($CaCl_3$), and recovered as an oil that was subjected to flash chromatography from toluene–ethyl acetate (9:1, v/v). The only substantial fraction supplied the *benzopyranone*, crystallising from ethanol as needles (471 mg, 31%), m.p. 145 °C, having a purple fluorescence in trichloromethane, ν_{max}/cm^{-1} 1640, 1630 (C=O), 1610, 1600 and 1565 (Found: C, 77.3; H, 4.75%; M^+, 264.080 13. $C_{17}H_{12}O_3$ requires C, 77.25; H, 4.6%; M^+, 264.078 63).

Oxidation with Triphenylcarbenium Perchlorate.—Triphenylcarbenium perchlorate (690 mg) in dichloromethane (10 cm^3) was added to the 9-methylbenzopyranobenzopyran **6b** (508 mg) in the same solvent (10 cm^3) to give, instantly, a red solution. Removal of the solvent *in vacuo* left a gum that solidified when rubbed with sodium–dry ether. This solid was thoroughly washed with dry ether to form a red powder (660 mg, 94%) identified as the methylbenzopyranobenzopyrylium perchlorate **1b** by ^1H NMR spectroscopy with deuteriotrichloromethane–trifluoroacetic acid as solvent; characteristic peaks from the isomeric salt **9b** were either absent or hardly detectable. The ether washings, which possessed almost no colour, contained triphenylmethane (450 mg, 92%), m.p. 92–94 °C, identified spectroscopically.

Acid-catalysed Dismutation of the Pyranopyran **6b**.—Treatment of the pyranopyran **6b** (50 mg) in trichloromethane (1 cm^3) with trifluoroacetic acid (0.1 cm^3) turned it instantly orange–red. The ^1H NMR spectrum was secured as rapidly as possible but indicated that change was already complete, no further change occurring during 3 days. Analysis of the spectrum of the mixture disclosed all peaks registered in Table 1 for the red and the yellow pyrylium salts **1b** and **9b** except those near δ 9.1 that were obscured by the solvent OH band. Relative intensities (peak heights) obtained at several points showed the red salt **1b** to be in a preponderance (ratio 2:1).

The spectrum contained a third series of signals almost entirely resolved from the salt signals and assigned to the dihydropyranopyran **10** in agreement with previous work.[2] The aromatic and methyl resonances are included in Table 1, but those emanating from the 6-H spin system need additional discussion. Since there was only one set of signals, only one (racemic; *trans*-fused) stereoisomer appeared to be present (very small long-range splittings were noted but not analysed). A broad, ill-resolved multiplet centred near δ 3.2 (theoretically 32 lines) is assigned to H_e though the splittings could not be assessed. In the OCH_2 group the geminal splitting J_{ab} is 10.9 Hz; H_a appears in the spectrum as a doublet of doublets, J_{ae} 3.2, centred at δ 4.53, while H_b appears as a 'triplet' with splitting J_{be} 11.3, centred at 4.00. The other methylene group resonates at higher field and is partly overlaid but the geminal splitting J_{cd} is 12.7, the larger value resulting from the adjacent benzene ring. A doublet of doublets centred at δ 2.84 can be assigned to H_d and a multiplet at about 2.53 (partly obscured by methyl bands) to H_c; of the two remaining splittings, only J_{cd} 10.8 could

be assessed with confidence. Finally, a doublet at δ 4.86 can be assigned only to H_f, with the single splitting J_{ef} 9.7 Hz. Even without allowing a reduction by *ca.* 2.5 Hz induced by the electronegative oxygen atom, this value is too large to correspond to a *cis*-fused ring junction whatever the conformation, but fits a *trans*-fused junction exactly. In particular, the conformation dictated by *trans*-fusion correctly identifies the high-field resonances in each geminal pair with the protons that experience large couplings to H_e because they are *trans* to it (and consequently in the shielding cones of the benzene rings). Previous workers[2] described what seems to be a different type of spectrum and concluded that the junction in their dihydropyranopyran must be *cis*. The dismutation of simpler benzopyrans is reported as giving mixtures of geometrical isomers in an irregular fashion,[7] so the two claims are not necessarily contradictory.

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