Flavonoid Epoxides. Part 18.[1] Solvolysis Products of 2-Arylmethylenebenzo[*b*]furan-3(2*H*)-one (Aurone) Epoxides

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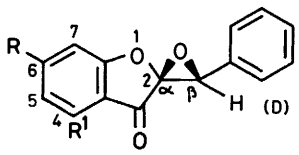
Aurone epoxides readily undergo solvolysis with aqueous acetone, methanol, and ethanol under neutral conditions, and also with acetic acid to give α,β-dihydroxy,α-hydroxy-β-alkoxy, and α-hydroxy-β-acetoxy aurones, which equilibrate in solution, through ring-chain tautomerism (Scheme 1), giving predominantly the cyclic benzofuranone diastereoisomers of the solvolysis products. Acetyl derivatives of the cyclic products and quinoxaline derivatives of the open-chain products have been prepared and characterised. Methanolysis of aurone epoxides under acid conditions gave α-methoxy-β-hydroxyaurone derivatives. ^{1}H N.m.r. spectroscopy was used in the tentative assignment of the configurations of the solvolysis products.

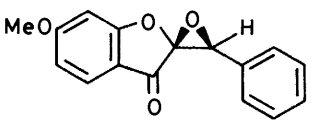
Aurone epoxides† are benzylic epoxides and accordingly readily undergo solvolysis with hydroxylic solvents.[2] Thus when the *Z*-aurone epoxide (**1**) was set aside in aqueous acetone at room temperature for 1 week and the *Z*-aurone epoxide (**2**) was heated under reflux in the same solvent system for 2 h, hydrolysis products (**5**) and (**7**) respectively were obtained. When the *Z*-aurone epoxides (**1**), (**2**), and (**3**) in methanol and the *Z*-aurone epoxide (**2**) in ethanol were heated under reflux for 2 h, the methanolysis products (**6**), (**8**), and (**11**), and the ethanolysis product (**9**) respectively were produced. In addition methanolysis of the *E*-aurone epoxide (**4**) gave the same product (**8**) as that obtained from methanolysis of the *Z*-isomer (**2**). The acetolysis product (**10**) was obtained on heating the epoxide (**2**) in acetic acid for 1 h.

Acetylation of compounds (**6**), (**8**), (**10**), and (**11**) with acetic anhydride–pyridine afforded, in each case, two diastereoisomeric products (**12a, b**), (**13a, b**), (**14a, b**), and (**15a, b**) in ratios of 66:34, 66:34, 56:44, and 66:34 respectively. The diacetates (**14a, b**) were also produced by the direct acetylation of glycol (**7**) (acetic anhydride–pyridine), and by treatment of the epoxide (**2**) with sodium acetate–acetic anhydride in ratios of 40:60 and 60:40 respectively. The configurational assignments of the diastereoisomers were based on ^{1}H n.m.r. analysis (see below).

A third possible isomeric acetyl derivative, that of the open-chain phenolic tautomer, was not detected (t.l.c. and n.m.r.) in the products of any of these acetylation reactions. That one of the two isomeric acetyl derivatives produced in each case was not the acetyl derivative of the phenolic open-chain isomer [*e.g.* (**8c**) in Scheme 1] was indicated by the small difference in the ^{1}H n.m.r. signals for the β-protons between the isomers of compounds (**12**)—(**15**) which were in the range 0.02—0.13 p.p.m. (see Table). The expected difference between a β-proton of one of these benzofuranone compounds and the corresponding proton in its possible open-chain α-diketone isomer is of the order of 0.7 p.p.m.



(**1**) R = R^1 = H
(**2**) R = OMe, R^1 = H
(**3**) R = R^1 = OMe



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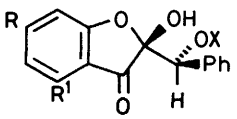
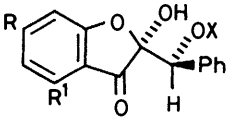
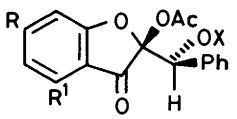


α*R*, β*S* (a)

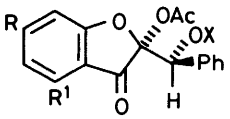


α*S*, β*S* (b)

(**5**) a or b; R = R^1 = H, X = H
(**6**) a or b; R = R^1 = H, X = Me
(**7**) a or b; R = OMe, R^1 = X = H
(**8**) a or b; R = OMe, R^1 = H, X = Me
(**9**) a or b; R = OMe, R^1 = H, X = Et
(**10**) a or b; R = OMe, R^1 = H, X = Ac
(**11**) a or b; R = R^1 = OMe, X = Me



α*S*, β*S* (a)



α*R*, β*S* (b)

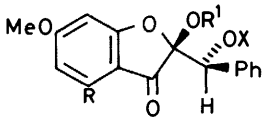
(**12**) a or b; R = R^1 = H, X = Me
(**13**) a or b; R = OMe, R^1 = H, X = Me
(**14**) a or b; R = OMe, R^1 = H, X = Ac
(**15**) a or b; R = R^1 = OMe, X = Me

Further, the ^{13}C n.m.r. spectra of the isomers of (**12**) (to take one example) are consistent with the benzofuranone structures but not with the open-chain α-diketone structure. The signals

† Nomenclature note.
2-Arylmethylenecoumaran-3-one or 2-arylmethylenebenzo[*b*]furan 3(2*H*)-one epoxides; the aurone nomenclature will be used in the discussion for convenience. The α and β prefixes refer to positions relative to the carbonyl group. The aurone epoxides and their derivatives described in this paper are racemates, only one enantiomer of which in each case is referred to in the text and is shown in the diagrams. The descriptors a and b as shown in the diagrams denote configurations of diastereoisomers. In earlier papers the terms *erythro* and *threo* respectively were used for these compounds.

for the C-3 carbonyl groups in the two isomers (**12a**) and (**12b**) occur at δ 196.5 and 194.8 and for the C-2 acetal carbons at δ 101.0 and 102.2, respectively. A second signal in the region expected for an α-diketone[3] is not present in these spectra. The two carbonyls of the α-diketone, benzil absorb at δ 194.3.[4]

When a solution of the epoxide (**2**) in methanol was treated with a trace of concentrated sulphuric acid and heated gently for 5 min, the methanolysis product (**8**) was again the main product



αR,βS (a)

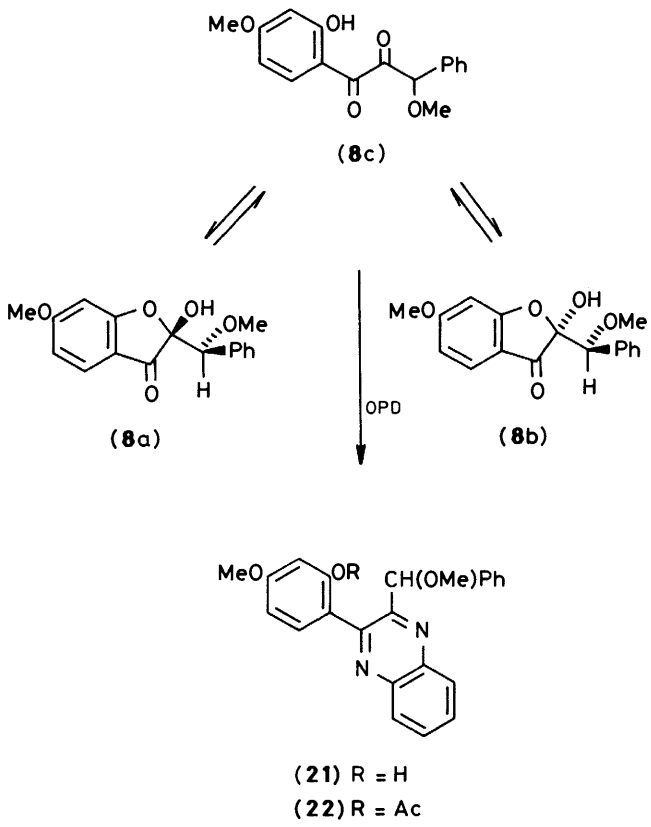
(**16**) R = H, R^1 = Me, X = H
(**17**) R = H, R^1 = Me, X = Ac
(**18**) R = H, R^1 = Et, X = H
(**19**) R = OMe, R^1 = Me, X = H
(**20**) R = OMe, R^1 = Me, X = Ac

(51%), but it was now accompanied by a smaller amount (6%) of the isomeric α-methoxy-β-hydroxy isomer (**16**). When the epoxide (**2**) in ethanol was similarly treated, the α-hydroxy-β-ethoxy (**9**) and α-ethoxy-β-hydroxy (**18**) products were obtained in yields of 67 and 3.5% respectively. The β-deuterio analogue (**2**; with β-D instead of β-H) gave similar results with methanol. A ^{1}H n.m.r. spectrum of the α-hydroxy-β-methoxy product showed that the entire deuterium content of starting epoxide had been lost; while that of the α-methoxy-β-hydroxy product (**16**; with β-D instead of β-H) showed, by the absence of a signal at δ 5.08 [β-H in (**16**)], that all of the deuterium had been retained.

That the opening of the epoxide ring occurred at the β-position (to the carbonyl group) of epoxides (**1**)—(**4**) on attack by the solvent in neutral solution to give products (**5**)—(**11**) was shown by the solubility of these products in aqueous sodium hydroxide, and by the exhibition of ring-chain tautomerism by the products in solution, as demonstrated by ^{1}H n.m.r. spectroscopy. 2-Benzyl-2-hydroxybenzo[*b*]furan-3(2*H*)-ones are known[5] to exhibit such properties. Products (**16**) and (**18**), in contrast, did not undergo ring-chain tautomerism and were insoluble in alkali. That the benzylic protons in these two compounds appeared as doublets (splitting by β-OH) in their respective n.m.r. spectra, whereas the benzylic protons in products (**6**) and (**8**)—(**11**) appeared as singlets, was further confirmation of the structures.

Under neutral, basic and, normally, under acid conditions epoxide ring opening is S_N2 in character.[6] In acid-catalysed epoxide ring opening, a modified S_N2 mechanism operates in which the transition state has a great deal of carbocation character as indicated by stereochemical evidence.[6] In the acid-catalysed methanolysis of the epoxides (**2**) and (**3**) where the solvent molecules attack the oxirane ring at the α-position to give the α-methoxy-β-hydroxy products (**16**) and (**19**) (as minor products), an S_N1 mechanism can be ruled out as this would involve the generation of a carbocation adjacent to the carbonyl group. Therefore, attack of these epoxides at the α-position must involve inversion of configuration at this centre to give the (α*R*,β*S*)-isomers (**16**) and (**19**). In the same way acid-catalysed ethanolysis of the epoxide (**2**) will give the (α*R*,β*S*)-ethanolysis product (**18**).

The configurations of the products (**5**)—(**11**) obtained on solvolysis of epoxides (**1**)—(**3**) under neutral conditions were not as readily determined because of the tautomerism which they undergo in solution. The stereochemistry of these products has been tentatively assigned by a comparison of their n.m.r. spectra to that of the (α*R*,β*S*)-benzofuranone (**16**), or to that of its acetate (**17**). Methanolysis products (**8a, b**) of the epoxide (**2**) and their acetates (**13a, b**) will be taken as examples for illustration.



(**21**) R = H
(**22**) R = Ac

Scheme 1. OPD = o-phenylenediamine

The expected mode of ring opening of the oxirane ring of the epoxide (**2**) on attack by methanol at the α-position is by way of an S_N2 mechanism[6] to give the (α*R*,β*S*)-α-hydroxy-β-methoxy diastereoisomer (**8a**). However, in solution the isomer (**8a**) was shown by n.m.r. spectroscopy to equilibrate with the corresponding isomer (**8b**) through the β-diketone (**8c**) (Scheme 1). The signals in the n.m.r. spectrum of a freshly prepared deuteriochloroform solution of the compound are shown for the isomer (**8a**) in the Table. This assignment will be discussed later. A spectrum taken of the same solution which had been left for some time (*ca.* 12 h) was much more complex. The new signals which appeared in the spectrum of the equilibrated solution are attributed to the isomer (**8b**) and are also shown in the Table.

In addition to these signals, low intensity signals at δ 11.67 and 5.55 become apparent at increased gain and are attributed to the phenolic and benzylic protons respectively of the α-diketone (**8c**). The methoxy and aromatic protons of this tautomer were masked by the signals of the isomers (**8a, b**). Integration of corresponding, well separated, signals of the isomers (**8a, b**) in the spectrum of the equilibrated deuteriochloroform solution indicated the presence of a 50:50 isomer ratio. When the solvents were acetone and dimethyl sulphoxide, the ratios of (**8a**):(**8b**) were 73:27 and 80:20 respectively. Signals due to the α-diketone open-chain tautomer (**8c**) were not observed when the spectra were taken in the latter two solvents.

That each isomer in the above mentioned spectra could be observed separately, and gave sharp resonance lines for various protons, indicated that the equilibrium between them was not established in less than 0.1 s at room temperature. That a true equilibrium was being observed rather than a mixture of

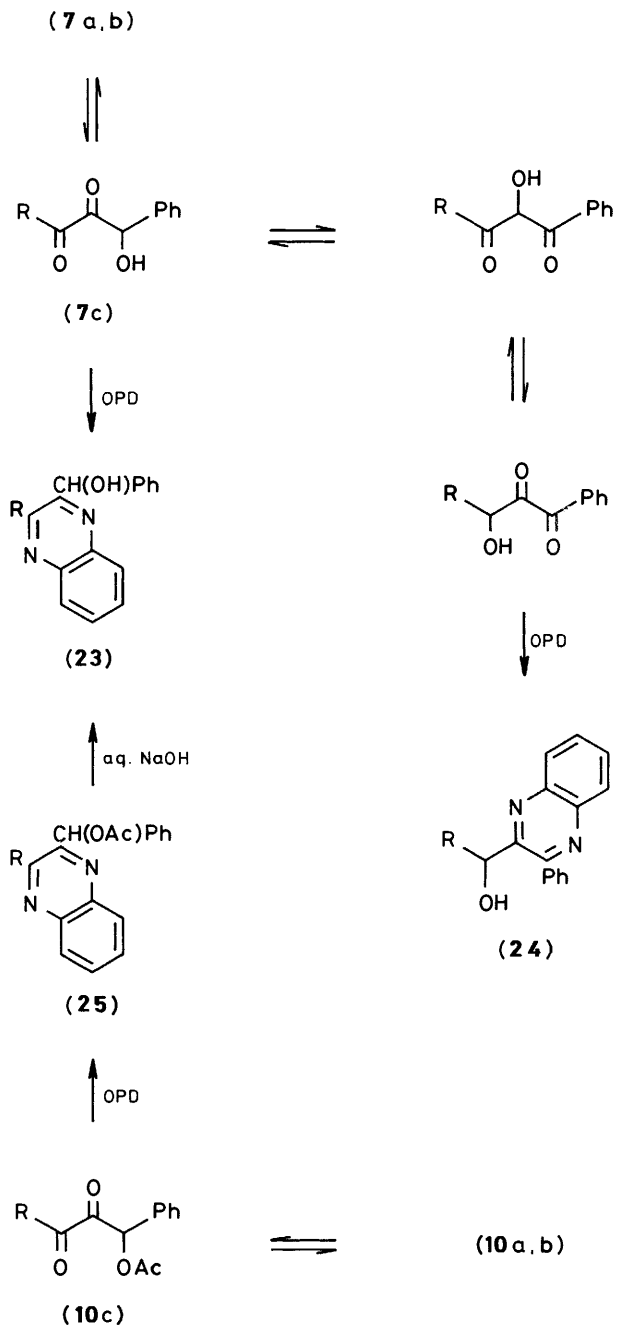
isomers was supported by the facts that; (i) the 'mixture' behaved as a single compound on t.l.c. plates; (ii) the position of equilibrium was found to be solvent dependent; (iii) successive recrystallization from a variety of solvents failed to effect a separation of isomers and the melting point remained constant at 134 °C; and (iv), the intermediate open chain α-diketone [*e.g.*, (**8c**) Scheme 1] could be trapped by a *o*-phenylenediamine to form the quinoxaline derivative (see below).

It may be inferred from the above observations, particularly from the fact that a freshly prepared solution of (**8**) in deuteriochloroform gave signals for isomer (**8a**), that the compound exists in this configuration (**8a**) in the crystalline state, and epimerises in solution to an extent dependent on the nature of the solvent. Isomer (**8b**) existed only in solution and was not obtained in the crystalline state. However, as reported above, the crystalline acetyl derivatives of both diastereoisomers were obtained from the acetylation of (**8**) by means of acetic anhydride and pyridine.

The quinoxaline derivative (**21**) of the intermediate open-chain tautomeric α-diketone (**8c**) was obtained in 50% yield on treatment of (**8**) with *o*-phenylenediamine in methanol at reflux temperature (Scheme 1). The quinoxaline was characterised through its acetyl derivative (**22**). In a similar reaction, the glycol (**7**) gave two isomeric quinoxalines (**23**) and (**24**) derived from two open-chain tautomers of the glycol (Scheme 2) in a ratio of 3:2. The quinoxalines were distinguished by independent synthesis of (**23**) through the formation of the quinoxaline derivative (**25**) of the open-chain tautomer of the α-hydroxy-β-acetoxy compound (**10**) followed by alkali deacetylation. It is noteworthy that Karrer and co-workers,[7] in the course of an investigation into the properties of dibenzoylcarbinols, found that the parent substance showed a marked tendency to enolise when dissolved in polar solvents. In no case was an isomeric 1,2-diketone isolated on ketonisation of the enols. These findings led the authors to the conclusion that the 1,3-diketone forms of dibenzoylmethanol were thermodynamically more stable than the isomeric 1,2-diketones. In the case of aurone glycols, however, there was no evidence, other than chemical, to show that the 1,2-diketone tautomer undergoes enolisation. However, the total loss of deuterium from the methanolysis product (**8**) of the β-deuterio analogue of the epoxide (**2**; β-D instead of β-H) would be possible through enolisation of the intermediate open-chain 1,2-diketo tautomer and such enolisation is implied in this case.

As mentioned earlier, the configurations of the solvolysis products of the aurone epoxides and of their derivatives have been assigned on the basis of a comparison of their ^{1}H n.m.r. spectra to that of the (α*R*,β*S*)-β-hydroxy-α-methoxy compound (**16**) or to that of its acetyl derivative (**17**) (see Table). For example, the δ-values for β-phenyl, 4-H, 5-H, 7-H listed for (α*R*,β*S*)-β-acetoxy-α-methoxy derivative (**17**) are in close agreement with those of the corresponding protons of the α,β-diacetoxy compound (**14a**) but not with those of its diastereoisomer (**14b**). Thus, these diastereoisomers were tentatively assigned the (a) and (b) configurations respectively as shown. The configurations of the diastereomeric α-acetoxy-β-methoxy compounds (**13a**, **b**) were similarly assigned. The δ values for the aromatic protons of a freshly prepared deuteriochloroform solution of the α-hydroxy-β-methoxy derivative (**8a**) also agree closely with those of derivative (**17**) but not the corresponding new signals in the equilibrated solution which are attributed to isomer (**8b**).

It was observed that, relative to the isomers having configurations (a)* the aromatic nuclei in the isomers with configurations (b) exert a mutual deshielding influence on each other. It was also noted that the signals of the protons of substituent groups on the α- and β-oxygen atoms occur at significantly higher field values in stereoisomers (a) compared to the corresponding protons of the stereoisomers (b). The magnitude of the difference for a given pair was of the order of 0.20—0.30 p.p.m. Further tentative assignments of configurations of compounds listed in the Table were made on the basis of these observations. Although the anisotropic effects discussed above are undoubtedly ascribable to different conformational requirements in each series of isomers, inspection of scale models of the isomers failed to afford an insight into the nature of these requirements, and it was not possible to assign a favoured conformation to any of the diastereoisomers.



Scheme 2. OPD = *o*-phenylenediamine, R = 2-HO, 4-MeOC$_6$H$_3$

* See page 1557.

Table. ^{1}H N.m.r. signals of some aurone epoxide derivatives

Compound	β-Ph[b]	4-H[c]	5-H[c]	7-H[c]	6-OMe	β-H	α-Substituent		β-Substituent	
(6a)[d]	7.50					4.60	OH	4.95	OMe	3.16
(6b)[d]	7.20					4.62	OH	4.95	OMe	3.44
(8a)	7.48	7.56 d	6.64 dd	6.57 d	3.87	4.57	OH	5.00	OMe	3.16
(8b)	7.23	7.32 d	6.47 dd	6.35 d	3.77	4.60	OH	5.00	OMe	3.42
(10a)[d]	7.45				3.89	6.04			OAc	1.92
(10b)[d]	7.28				3.83	6.11			OAc	2.17
(11a)[e]	7.40		6.13 d	6.27 d	*f*	4.40	OH	7.61	OMe	2.98
(11b)[e]	7.24		6.02 d	6.20 d	*f*	4.45	OH	7.72	OMe	3.17
(12a)[d]	7.55	7.65 dd				4.62	OAc	1.94	OMe	3.10
(12b)[d]	7.23	7.4 dd				4.58	OAc	2.13	OMe	3.34
(13a)	7.50	7.65 d	6.70 dd	6.55 d	3.90	4.63	OAc	1.98	OMe	3.16
(13b)	7.15	7.22 d	6.38 dd	6.28 d	3.75	4.50	OAc	2.09	OMe	3.33
(14a)	7.41	7.59 d	6.65 dd	6.54 d	3.84	6.10	OAc	1.86 or 1.97	OAc	1.86 or 1.97
(14b)	7.25	7.39 d	6.55 dd	6.45 d	3.82	6.19	OAc	2.09 or 2.12	OAc	2.09 or 2.12
(15a)	7.54		6.15 d	6.25 d	*f*	4.67	OAc	1.96	OMe	3.17
(15b)			5.95 d	6.15 d	*f*	4.65	OAc	2.12	OMe	3.41
(16)	7.40	7.49 d	6.56 dd	6.53 d	3.85	5.08 d[g]	OMe	3.23	OH	2.61 d[g]
(17)	7.40	7.56 d	6.66 dd	6.59 d	3.90	6.08	OMe	3.19	OAc	1.86
(19)[e]	7.35		6.15 d	6.37 d	*f*	4.74 d[g]	OMe	2.99	OH	5.71 d[g]
(20)[s]	7.40				*f*	6.04	OMe	3.20	OAc	1.90

> In δ values relative to TMS in $CDCl_3$ unless otherwise stated. [b] When multiplets, the mean values are given. [c] Doublets (d): *ortho*-coupling, *J* 8—9 Hz; *meta*-coupling, *J* 2—2.5 Hz; *p*-coupling, *J* ~ 1 Hz. [d] A-Ring protons not fully resolved. [e] $(CD_3)_2SO$ as solvent. [f] The signals for the 4-and 6-OMe groups were not distinguished: for (**11a**), both at 3.84, for (**11b**), both at 3.74, for (**15a**) at 3.99 and 3.90; for (**15b**) both at 3.84, for (**19**) at 3.84 and 3.81, for (**20**) at 3.92 and 3.91. [g] (d) *ca* 5 Hz.

Experimental

^{1}H N.m.r. spectra were recorded on a Varian HR 60 A spectrometer and ^{13}C n.m.r. spectra on a JEOL GX 270 spectrometer in deuteriochloroform (unless otherwise stated) with $SiMe_4$ as internal reference. I.r. spectra were recorded on a Beckman IR 5 spectrometer. For many of the ^{1}H n.m.r. values see the Table.

(αR,βS; αS,βR)-2-*Hydroxy*-2-(α-*hydroxybenzyl*)*benzo*[b]-*furan*-3(2H)-*one* (**5a**).—A solution of the *Z*-aurone epoxide (**1**),[18] (1 g) in aqueous acetone (20:80; 100 ml) was kept at room temperature for 1 week. The solid which separated was collected and recrystallised from chloroform–ligroin to give colourless needles of the *hydrolysis product* (**5a**) (0.25 g, 24%), m.p. 96—98 °C (Found: C, 70.0; H, 4.9. $C_{15}H_{12}O_4$ requires C, 70.30; H, 4.72%); δ(Me_2CO; freshly prepared solution), 4.68 (d, *J* 5 Hz, β-OH), 5.09 (d, 5 Hz, β-H) and 6.39 (s, α-OH); with time, the solution gave additional signals, attributed to the isomer (**5b**), at δ 5.07 (β-OH), 5.07 (β-H), and 6.61 (α-OH).

(αR,βS; αS,βR)-2-*Hydroxy*-2-(α-*hydroxybenzyl*)-6-*methoxy*-*benzo*[b]*furan*-3(2H)-*one* (**7a**).—A solution of *Z*-aurone epoxide (**2**),[18] (0.5 g) in aqueous acetone (20:80; 100 ml) was heated under reflux for 2 h. The solution was evaporated to a quarter of its volume and allowed to cool. The solid which separated was collected and recrystallised from aqueous ethanol to give colourless crystals of the *hydrolysis product* (**7a**) (0.4 g, 75%), m.p. 152—153 °C (Found: C, 67.15; H, 5.1. $C_{16}H_{14}O_3$ requires C, 67.12; H, 4.93%); $\nu_{max.}$(Nujol) 3 333 and 1 695 cm^{-1}; δ(Me_2CO; freshly prepared solution) 3.91 (s, 6-OMe), 4.62 (d, *J* 5 Hz, β-OH), 5.03 (d, *J* 5 Hz, β-H), and 6.32 (s, α-OH); δ(DMSO) 5.57 (d, *J* 5 Hz, β-OH) and 7.60 (s, α-OH); δ(Me_2CO; with time) gave additional signals, attributed to isomer (**7b**), at 3.86 (6-OMe), 5.02 (β-OH), 5.02 (β-H), and >6.32 (α-OH); δ(DMSO), 4.83 (d, *J* 5 Hz, β-H), 5.82 (d, *J* 5 Hz, β-OH), and 7.72 (α-OH).

(αR,βS; αS,βR)-2-*Hydroxy*-2-(α-*methoxybenzyl*)*benzo*[b]-*furan*-3(2H)-*one* (**6a**).—A solution of the epoxide (**1**) (0.2 g) in absolute methanol (12 ml) was heated under reflux for 2 h and allowed to cool. The solid which separated on dilution with ice–water crystallised from methanol as colourless hexagonal plates of the *methanolysis product* (**6a**) (0.18 g, 80%), m.p. 131—132 °C (Found: C, 71.4; H, 5.25. $C_{16}H_{14}O_4$ requires C, 71.10; H, 5.22%); $\nu_{max.}$(KBr) 3 333 and 1 713 cm^{-1}.

(αR,βS; αS,βR)-2-*Hydroxy*-6-*methoxy*-2-(α-*methoxybenzyl*)-*benzo*[b]*furan*-3(2H)-*one* (**8a**).—In a similar experiment, the epoxide (**2**) gave colourless needles (from aqueous methanol) of the *methanolysis product* (**8a**) (77%), m.p. 134 °C (Found: C, 68.2; H, 5.5. $C_{17}H_{16}O_5$ requires C, 67.97; H, 5.54%).

(αR,βS; αS,βR)-2-*Hydroxy*-4,6-*dimethoxy*-2-(α-*methoxy*-*benzyl*)*benzo*[b]*furan*-3(2H)-*one* (**11a**).—In a similar experiment the epoxide (**3**) gave colourless needles (from ethanol) of the *methanolysis product* (**11a**) (85%), m.p. 153—154 °C (Found: C, 65.4; H, 5.6. $C_{18}H_{18}O_6$ requires C, 65.44; H, 5.49%).

(αR,βS; αS,βR)-2-(α-*Ethoxybenzyl*)-2-*hydroxy*-6-*methoxy*-*benzo*[b]*furan*-3(2H)-*one* (**9a**).—In a similar experiment in which ethanol replaced methanol, the epoxide (**2**) gave the *ethanolysis product* (**9a**) (83%) as colourless needles (aqueous ethanol), m.p. 112—114 °C (Found: C, 66.6; H, 5.8. $C_{18}H_{18}O_5 \cdot \frac{1}{2}H_2O$ requires C, 66.91; H, 5.86%); $\nu_{max.}$(KBr) 3 333 and 1 684 cm^{-1}; δ($CDCl_3$; freshly prepared solution), 0.98 (t, *J* 7.4 Hz, OCH_2CH_3), 3.42 (q, *J* 7.4 Hz, OCH_2CH_3), 3.86 (6-OMe), 4.69 (β-H) and 5.10 (br, α-OH); with time the solution gave additional signals, attributed to the isomer (**9b**), at δ 1.27 (t, *J* 7.4 Hz, OCH_2CH_3), 3.45 (q, *J* 7.4 Hz, OCH_2CH_3), 3.74 (6-OMe), 4.70 (β-H), and 5.10 (α-OH, br).

(αR,βS; αS,βR)-2-(α-*Acetoxybenzyl*)-2-*hydroxy*-6-*methoxy*-*benzo*[b]*furan*-3(2H)-*one* (**10a**).—A solution of the epoxide (**2**) (0.5 g) in acetic acid (25 ml) was kept at 100 °C for 1 h. The cooled solution was diluted with water to give a crude off-white solid which was purified by p.l.c. (Merck silica gel G; benzene)

and crystallised from chloroform–ligroin to give colourless needles of the *acetolysis product* (**10a**) (0.45 g, 75%), m.p. 108—110 °C (Found: C, 65.8; H, 5.3. $C_{18}H_{16}O_6$ requires C, 65.85; H, 4.91%); $\nu_{max.}$ 3 389, 1 751 and 1 710 cm^{-1}.

(αS,βS; αR,βR)- *and* (αR,βS; αS,βR)-2-*Acetoxy*-2-(α-*methoxybenzyl*)*benzo*[b]*furan*-3(2H)-*one* (**12a**) *and* (**12b**).—A mixture of the courmaranone (**6**) (0.2 g), acetic anhydride (3 ml), and dry pyridine (0.1 ml) was kept at room temperature for 12 h. The solution was poured into water, and the resulting solid * was collected and washed with water. The isomeric products were separated by p.l.c. (Merck silica gel G, methylene dichloride). The upper band was extracted with chloroform and yielded an oil which crystallised from methanol as colourless needles of the *acetate* (**12a**) (0.11 g, 50%), m.p. 118—119 °C (Found: C, 69.55; H, 5.15. $C_{18}H_{16}O_5$ requires C, 69.22; H, 5.16%); $\nu_{max.}$(KBr) 1 770 and 1 740 cm^{-1}; δ_H (see Table); δ_C 20.24 ($COCH_3$), 57.50 (OCH_3), 83.84 (β-C), 101.02 (C-2), 112.16 (C-7), 121.82 (C-3a), 122.33 (C-4 or C-5), 123.79 (C-4 or C-5), 128.05, 128.85, 128.91 (β-Ph; C-2′,3′,4′,5′,6′), 134.70 (β-Ph; C-1′), 137.50 (C-6), 167.66 (C-7a or $OCOCH_3$), 170.88 (C-7a or $OCOCH_3$), and 196.50 (C-3).

Similar treatment of the lower band gave a solid which crystallised from methanol as colourless plates of the *acetate* (**12b**) (0.05 g, 23%), m.p. 148—149 °C (Found: C, 69.4; H, 5.3. $C_{18}H_{16}O_5$ requires C, 69.22; H, 5.16%); $\nu_{max.}$(KBr) 1 762 and 1 740 cm^{-1}; δ_C 20.41 ($OCOCH_3$), 58.30 (OCH_3), 83.98 (β-C), 102.10 (C-2), 112.02 (C-7), 121.35 (C-3a), 122.26 (C-4 or C-5), 123.86 (C-4 or C-5), 127.91 and 128.79 (β-Ph; C-2′,3′,4′,5′,6′), 133.15 (β-Ph; C-1′), 137.58 (C-6), 168.22 (C-7a or $OCOCH_3$), 169.63 (C-7a or $OCOCH_3$), and 194.78 (C-3).

(αS,βS; αR,βR)- *and* (αR,βS; αS,βR)-2-*Acetoxy*-6-*methoxy*-2-(α-*methoxybenzyl*)*benzo*[b]*furan*-3(2H)-*one* (**13a**) *and* (**13b**).—The coumaranone (**8**) was acetylated and worked up as for coumaranone (**6**) above, to yield colourless needles (ethanol) of the acetate (**13a**) (53%), m.p. 164—165 °C (Found: C, 66.9; H, 5.6. $C_{19}H_{18}O_6$ requires C, 66.66; H, 5.30%); $\nu_{max.}$(KBr) 1 770 and 1 723 cm^{-1}; and the acetate (**13b**) (26%) as colourless plates (ethanol), m.p. 161—162 °C (Found: C, 66.9; H, 5.25. $C_{19}H_{18}O_6$ requires C, 66.66; H, 5.30%).

(αS,βS; αR,βR)- *and* (αR,βS; αS,βR)-2-*Acetoxy*-4,6-*dimethoxy*-2-(α-*methoxybenzyl*)*benzo*[b]*furan*-3(2H)-*one* (**15a**) *and* (**15b**).—The coumaranone (**11**) was acetylated and worked up as for coumaranone (**6**) above, to yield colourless cubes (ethanol) of the *acetate* (**15a**) (55%), m.p. 208 °C (Found: C, 64.75; H, 5.7. $C_{20}H_{20}O_7$ requires C, 64.51; H, 5.41%); $\nu_{max.}$(KBr) 1 774 and 1 728 cm^{-1}; and an oil (23%) which failed to crystallise from the usual solvents, but was characterised as the acetate (**15b**) from its n.m.r. spectrum (see Table).

(αS,βS; αR,βR)- *and* (αR,βS; αS,βR)-*2-Acetoxy*-2-(α-*acetoxybenzyl*)-6-*methoxybenzo*[b]*furan*-3(2H)-*one* (**14a**) *and* (**14b**).—*Method* (*a*). The coumaranone (**10**) was acetylated and worked up as for the coumaranone (**6**) above, to yield colourless needles (ethanol) of the diacetate (**14a**) (30%), m.p. 161 °C (Found: C, 64.5; H, 4.7. $C_{20}H_{16}O_7$ requires C, 64.86; H, 4.90%); $\nu_{max.}$ 1 760 and 1 724 cm^{-1}; and colourless cubes (ethanol) of the diacetate (**14b**), (40%) m.p. 144—145 °C (Found: C, 65.15; H, 4.9. $C_{20}H_{18}O_7$ requires C, 64.86; H, 4.90%); $\nu_{max.}$ 1 764 and 1 729: cm^{-1}.

Method (*b*). The glycol (**7**) was acetylated as for the coumaranone (**6**) to yield the diacetate (**14a**) and the diacetate (**14b**) in a ratio of 40:60 (n.m.r.).

* Integration of the areas under the acetate signals in the ^1H n.m.r. spectrum gave an isomer distribution of 66% (**12a**) and 34% (**12b**).

Method (*c*). A mixture of the epoxide (**2**) (0.25 g), sodium acetate (0.1 g), and acetic anhydride (10 ml) was heated at 100 °C for 1 h. The cooled reaction mixture was poured into water and the solid product was separated by fractional crystallisation from ethanol to give the diacetate (**14a**) (53%), m.p. and mixed m.p. 161 °C, and the diacetate (**14b**), (35%), m.p. and mixed m.p. 144—145 °C.

Acid-catalysed Solvolysis of Epoxides: General Procedure.—A mixture of the epoxide (0.2—3 g), the appropriate solvent (20 to 200 ml), and conc. sulphuric acid (0.1—0.8 ml) was heated gently on a steam-bath for 5 min. The cooled solution was diluted with water and extracted with ether. The ethereal solution was extracted with aqueous sodium hydrogen carbonate (5%) and with sodium hydroxide (5%). It was then washed with water and dried ($CaSO_4$).

The product obtained on acidification of the sodium hydroxide extract was recrystallised from aqueous methanol to give the 2-hydroxy product. The product obtained on evaporation of the solvent from the ether phase was recrystallised from the appropriate solvent to give the 2-alkoxy product.

The epoxide (**2**) in methanol gave the 2-hydroxy product (**8**) (51%), m.p. and mixed m.p. 134 °C, and colourless needles (from methanol) of the 2-methoxy product, (αR,βS; αS,βR)-2-(α-*hydroxybenzyl*)-2,6-*dimethoxybenzo*[b]*furan*-3(2H)-*one* (**16**) (6%), m.p. 171—172 °C (Found: C, 67.6; H, 5.3; OMe, 20.3. $C_{17}H_{16}O_5$ requires C, 67.99; H, 5.37; OMe, 20.69%); $\nu_{max.}$ 3 415 and 1 695 cm^{-1}. *Acetyl derivative* (**17**) (pyridine–acetic anhydride), m.p. 154—155 °C (Found: C, 67.0; H, 5.3. $C_{19}H_{18}O_6$ requires C, 66.66; H, 5.30%); $\nu_{max.}$ 1 754 and 1 724 cm^{-1}.

The (Z)-6-*methoxy*[β-^{2}H]*aurone epoxide*[8] [epoxide (**2**); with the β-H replaced by deuterium] in methanol gave the 2-hydroxy product (**8**), m.p. and mixed m.p. 134 °C (an n.m.r. spectrum showed the complete absence of deuterium); and (αR,βS; αS,βR)-2,6-*dimethoxy*-2-(α-[^{2}H]*hydroxybenzyl*)*furan*-3(2H)-*one*, m.p. 171—172 °C alone or when mixed with a non-isotopic sample. The absence of a signal at δ 5.08 [*cf.* spectrum (**16**) in the Table] confirmed the presence of a benzylic deuteron.

The Epoxide (**2**) in ethanol afforded the 2-hydroxy product (**9**) (67%), m.p. and mixed m.p. 112—115 °C, and colourless needles (from aqueous ethanol) of (αR,βS; βS,αR)-2-*ethoxy*-2-(α-*hydroxybenzyl*)-6-*methoxybenzo*[b]*furan*-3(2H)-*one* (**18**) (3.5%), m.p. 100—101 °C (Found: C, 68.4; H, 5.95. $C_{18}H_{18}O_5$ requires C, 68.78; H, 5.77%); δ 1.14 (t, *J* 7 Hz, OCH_2CH_3), 2.74 (d, *J* 5 Hz, β-OH), 3.49 (q, *J* 7 Hz, OCH_2CH_3), 3.87 (s, 6-OMe), and 5.10 (d, *J* 5 Hz, β-H).

The epoxide (**3**)[8] in methanol yielded the 2-hydroxy product (**11**) (55%), m.p. and mixed m.p. 153—154 °C, and colourless needles from ethanol of (α*R*,β*S*; α*S*,β*R*)-2-(α-*hydroxybenzyl*)-2,4,6-*trimethoxybenzo*[b]*furan*-3(2*H*)-*one* (**19**) (14%), m.p. 201—202 °C (lit.,[9] m.p. 201—203 °C), the m.p. showed no depression when admixed with a sample of compound (**19**) prepared by the alkaline hydrogen peroxide oxidation of 2′-hydroxy-α,4′,6′-trimethoxychalcone;[9] $\nu_{max.}$(Nujol) 3 367 and 1 693 cm^{-1}. The *acetyl derivative* (**20**) (pyridine–acetic anhydride), had m.p. 203—204 °C (Found: C, 64.85; H, 5.6. $C_{20}H_{20}O_7$ requires C, 64.50; H, 5.41%); $\nu_{max.}$(KBr) 1 742 and 1 702 cm^{-1}.

Quinoxalines (**21**) *and* (**22**).—A mixture of the coumaranone (**8**) (0.162 g), *o*-phenylenediamine (0.06 g) and methanol (25 ml) was heated under reflux for 1 h. The solid obtained on dilution with water was collected, washed with aqueous sulphuric acid (1%) and water, and crystallised from aqueous methanol to give colourless prisms of 2-(2-*hydroxy*-4-*methoxyphenyl*)-3-(α-*methoxybenzyl*)*quinoxaline* (**21**) (0.1 g, 50%), m.p. 114—124 °C (decomp.); it was characterised through its acetate. Thus, a mixture of the quinoxaline (**21**) (0.5 g), acetic anhydride (25 ml),

and sodium acetate (1 g) was heated under reflux for 2 h. On work-up it gave colourless prisms (methanol) of 2-(2-*acetoxy*-4-*methoxyphenyl*)-3-(α-*methoxybenzyl*)*quinoxaline* (0.45 g, 80%), m.p. 112 °C (Found: C, 72.35; H, 5.45; N, 6.65. $C_{25}H_{22}N_2O_4$ requires C, 72.45; H, 5.35; N, 6.76%); $\nu_{max.}$(KBr) 1 765 cm^{-1}.

Quinoxalines (**23**) *and* (**24**).—The coumaranone (**7**) (0.5 g) was treated with *o*-phenylenediamine (0.2 g) as for the coumaranone (**8**) above. The solid product was separated by p.l.c. (Merck silica gel G, benzene–ether). The upper band was extracted with chloroform to yield a yellow solid which afforded on crystallisation from ethanol fluffy yellow needles of 2-(2-*hydroxy*-4-*methoxyphenyl*)-3-(α-*hydroxybenzyl*)*quinoxaline* (**23**) (0.3 g, 48%); m.p. 245—246 °C (Found: C, 73.3 H, 4.95; N, 8.45. $C_{22}H_{18}N_2O_3$ requires C, 73.73; H, 5.06; N, 7.82%).

Similar treatment of the lower band gave a solid which on crystallisation from ethanol afforded yellow needles of 2-*phenyl*-3-(α,2-*dihydroxy*-4-*methoxybenzyl*)*quinoxaline* (**24**), m.p. 172—173 °C (Found: C, 74.1; H, 5.2; N, 7.55. $C_{22}H_{18}N_2O_3$ requires C, 73.73; H, 5.06; N, 7.82%).

Quinoxaline (**25**).—A solution of the coumaranone (**10**) (0.1 g) and *o*-phenylenediamine (0.034 g) in chloroform (25 ml) was kept over anhydrous sodium sulphate (0.5 g) for 12 h. The oil obtained on work-up was purified by p.l.c. (Merck silica gel HF, methylene dichloride) to give a pale yellow oil of 3-(α-*acetoxybenzyl*)-2-(2-*hydroxy*-4-*methoxyphenyl*)*quinoxaline* (**25**) (80 mg, 66%); δ 2.12 (s, OAc), 3.82 (s, OMe), 6.62 (s, α-H), and 2.66 (s, Ph). The phenolic proton was buried in the aromatic region. The oil decomposed with time. It was characterised by hydrolysis at reflux temperature for 30 min in aqueous methanolic sodium hydroxide to give the quinoxaline (**23**) as fluffy yellow needles from ethanol, m.p. and mixed m.p. 245—246 °C.

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