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# Flavonoid Epoxides. Part 20.[1] Some Unusual Reactions of Dimethyldioxirane (DMD) with Flavonoid Compounds

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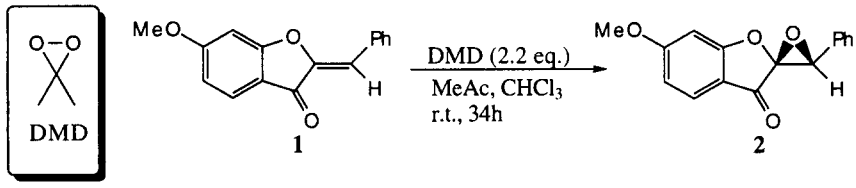
***Abstract:*** Dimethyldioxirane (DMD), generally as a solution in acetone, has proved itself to be an excellent epoxidising agent. It was observed that either the 2'-hydroxychalcone epoxide or the *trans*-2,3-dihydroflavonol could be obtained depending on the pH of the reaction mixture and the type of β-arene ring present in the substrate. Using this methodology *trans*-2,3-dihydroflavonols can be synthesised in far better yields than by the most commonly used method for their synthesis, that of the Algar-Flynn-Oyamada reaction. Treatment of both flavonol **14** and the novel isoaurone **21** with DMD gave unusual products instead of the expected epoxides, but nonetheless, an epoxide was assumed to have formed during the reaction. © 1997 Elsevier Science Ltd.

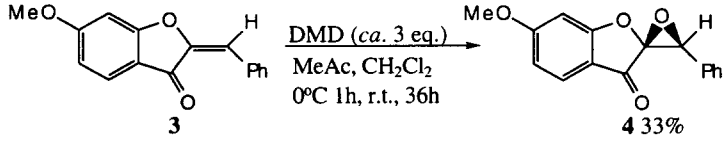
Over the last number of years dimethyldioxirane (DMD), particularly as a solution in acetone, has proved itself time and again to be a very useful epoxidising agent,[3] forming epoxides in good yields where other more traditional methods *e.g.* mCPBA and alkaline hydrogen peroxide, *etc.*, have failed or only afforded such products in poor yields. Indeed, Adam *et al.*[4] were the first to show the successful epoxidation of flavones in almost quantitative yields and later the epoxidation of both aurones[5] and chalcones[6] to their epoxides in quantitative yields.

At this period of time, we too, were also working on epoxidation reactions with flavonoid substrates and we obtained some interesting results which we wish to report now.

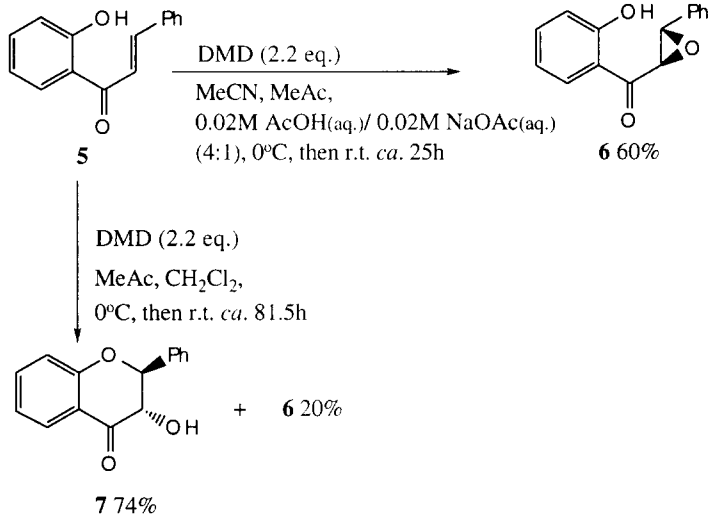
Since we were interested in improving the yield of (*Z*)-6-methoxyaurone epoxide[7] **2**, an intermediate in the synthesis of the glycolic acid **20** (see below), available previously in 58% yield by treatment of **1** with alkaline hydrogen peroxide.[8] We found that epoxidation of (*Z*)-6-methoxyaurone **1** gave the corresponding (*Z*)-6-methoxyaurone epoxide **2** (*trans*-6-methoxyaurone epoxide) in quantitative yield.



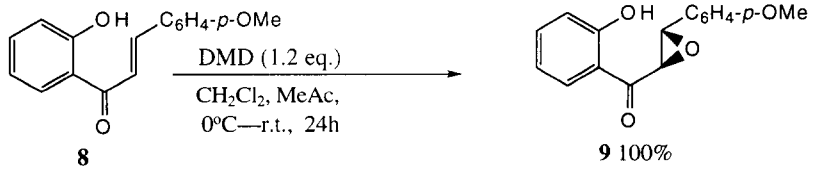

When we turned our attention to (*E*)-6-methoxyaurone **3**[9] and treated it with DMD in acetone, it gave a mixture of (*E*)-6-methoxyaurone epoxide **4**[10] (33%) and starting material **3** (67%).



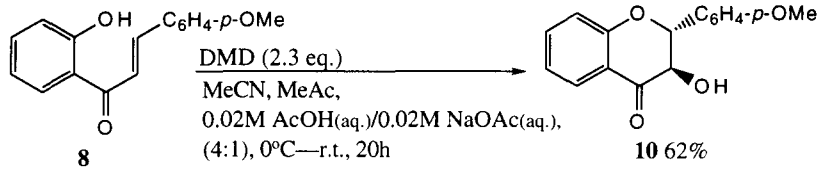
Unsubstituted (*E*)-2'-hydroxychalcone **5** was epoxidised by dimethyldioxirane to give the corresponding epoxide **6** in 60% yield, when the reaction was carried out at 0°C to room temperature over a period of 25 h, in a reaction medium buffered (AcOH/NaOAc) to a pH of *ca.* 4.4. This method represents a significant improvement on that of Ramakrishnan and Kagan,[11] who obtained the epoxide **6** in only 20% yield using mCPBA in refluxing chloroform. Prior to this experiment, epoxidation of the chalcone **5** using dimethyldioxirane was attempted at approximately neutral pH. It afforded 2,3-dihydroflavonol **7** in 74% yield, along with unreacted starting material **5** (5%) and 2'-hydroxychalcone epoxide **6** in 20% yield (this yield was determined from the $^1$H nmr spectrum of the crude reaction product as this epoxide decomposed during chromatography). This was not surprising in the light of the work of Adams and Main[12] who established that 2'-hydroxychalcone epoxides were stable at pH's of *ca.* 4.4. When the pH was increased to neutral, these workers observed that cyclisation of the (*E*)-2'-hydroxychalcone epoxide **6** to the *trans*-2,3-dihydroflavonol **7** had occurred.[13]




Treatment of (*E*)-2'-hydroxy-4-methoxychalcone **8** with dimethyldioxirane in acetone afforded the corresponding epoxide **9** in quantitative yield.

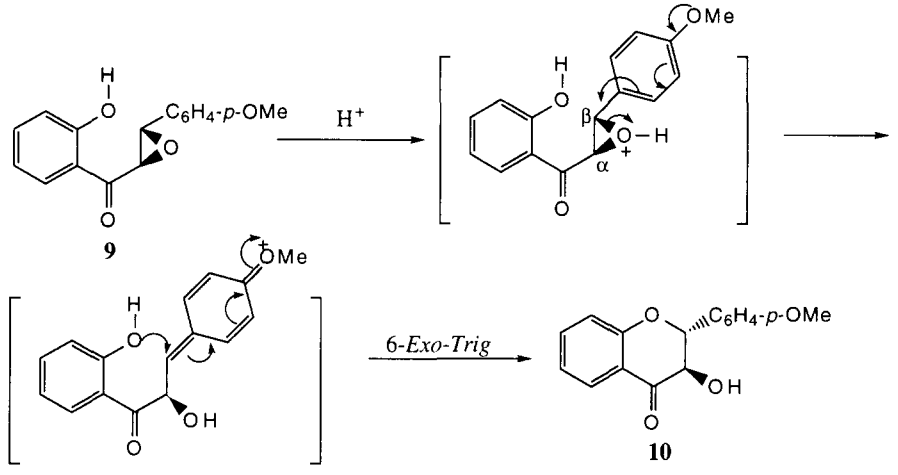



When this epoxide **9** was heated in methanol it cyclised to the corresponding *trans*-2,3-dihydroflavonol **10**. Surprisingly, when (*E*)-2'-hydroxy-4-methoxychalcone **8** was treated with dimethyldioxirane in acetone in the presence of an acetic acid/sodium acetate buffer system (pH *ca.* 4.4), *trans*-2,3-dihydroflavonol **10** was obtained in an isolated yield of 62%. To explain why the 2,3-dihydroflavonol **10** was obtained




**8** **10** 62%

when the reaction medium was buffered to a pH of *ca.* 4.4, it was suggested that the chalcone epoxide **9** which was assumed to be an intermediate in this reaction, was protonated and underwent a favourable 6-*Exo-Trig*[14] cyclisation (as shown in Scheme 1) to give the 2,3-dihydroflavonol **10**. It was hypothesised that cyclisation readily occurs because of the activating effect of the *p*-methoxyphenyl substituent.

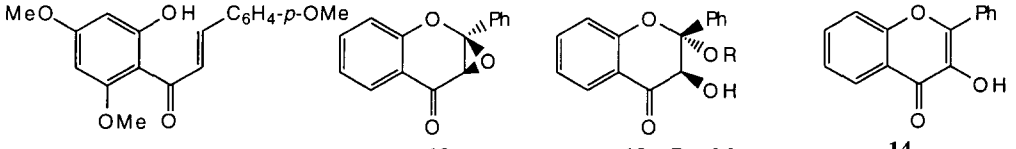



**9** **10**

Scheme 1

The above represents an important advance in the synthesis of *trans*-2,3-dihydroflavonols because up till now they were usually synthesised in poorer yields by the Algar-Flynn-Oyamada reaction[15a] or by the modified version of Saxena *et. al.* [15b]

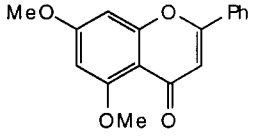
Treatment of (*E*)-2'-hydroxy-4,4',6'-trimethoxychalcone **11** with dimethyldioxirane in acetone with or without an acetic acid/sodium acetate buffer system (pH *ca.* 4.4) gave only starting material (22%) and saturated decomposition material (as indicated from $^1$H nmr spectroscopy) in the former case and an intractable mixture of compounds in the latter case.



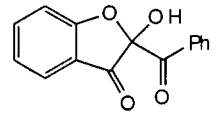

**11** **12** **13a** R = Me **13b** R = Ac **14**

Flavone epoxide **12** was synthesised according to the procedure of Adam *et al.*[4] and neither of the solvolysis products **13a** or **13b** were isolated upon treatment with methanol and acetic acid, respectively, only flavonol **14** was obtained in each case.

An attempt was also made at epoxidising 5,7-dimethoxyflavone **15**[16] with dimethyldioxirane in acetone, as it has never before been epoxidised. However, this reaction furnished an intractable mixture of compounds that was not investigated any further. It would appear that, as in the case of (*E*)-2'-hydroxy-4,4',6'-trimethoxychalcone **11**, that dimethyldioxirane is over-reactive with this substrate.

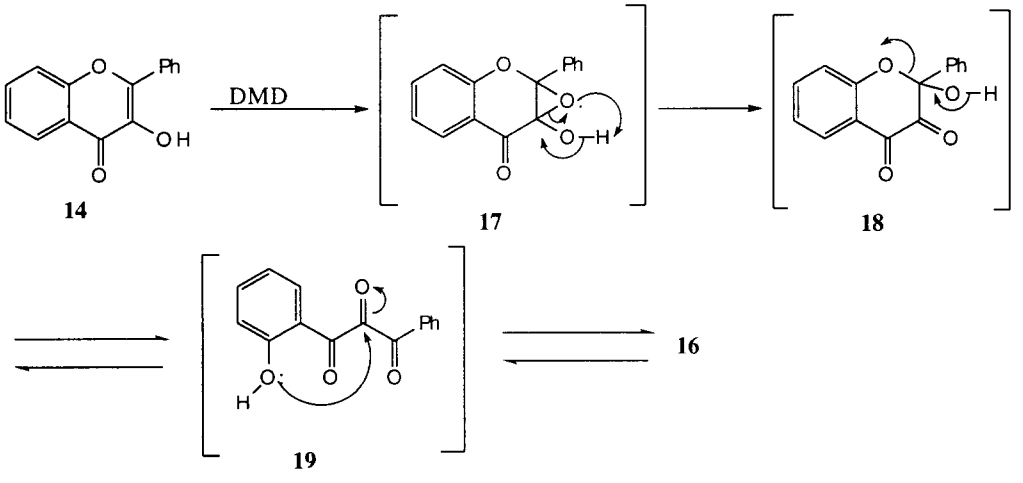



**15**




**16**

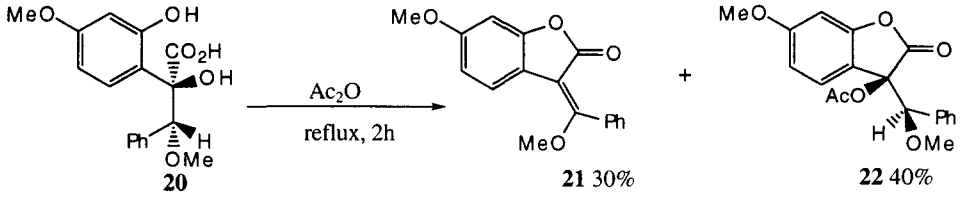
An effort was made at converting unsubstituted flavonol **14** to its corresponding epoxide with dimethyldioxirane. However, 2-benzoyl-2-hydroxybenzofuran-3-one **16** was isolated in 56% yield and no trace of the epoxide was observed. This result is not at all surprising since flavonol **14** has been oxidised to 2-benzoyl-2-hydroxybenzofuran-3-one **16** using periodic acid by Smith[17a] and copper (II) chloride under an atmosphere of oxygen by Utaka and Takeda.[17b] It was proposed in the case of dimethyldioxirane oxidation of flavonol, that an epoxide intermediate **17** (Scheme 2) was formed, which rearranged to the benzofuran-3-one **16** in the manner delineated in the Scheme. That a 1,2,3-triketone **19** was involved in this reaction mechanism has also been suggested by Smith,[17a] when studying periodate oxidation of flavonols. However, no reference to the intermediacy of a flavonol epoxide was made in the earlier cases.[17a,b] It is quite probable that the benzofuran-3-one **16** can ring-chain tautomerise to the flavandione **18** as suggested by Smith.[17a] However, this could not be confirmed by $^1$H nmr spectroscopy (270 MHz), due to the considerable complexity of the spectrum.




**14** **17** **18** **19**

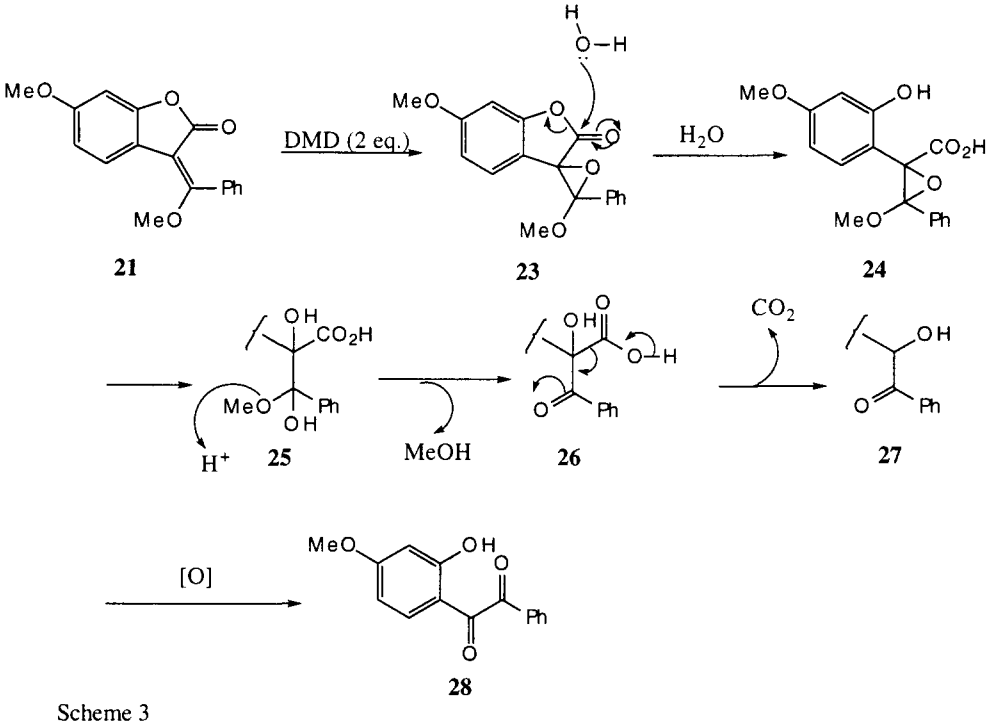
Scheme 2

(*E*)-3-(α-methoxybenzylidene)-6-methoxybenzofuran-2(3H)-one **21**[18] which was synthesised from (2*R*, 3*R*)-2-hydroxy-2-(2-hydroxy-4-methoxyphenyl)-3-methoxy-3-phenylpropan-1-oic acid **20**[1] (as shown below), was treated with DMD as a solution in acetone[19], but instead of giving the desired isoaurone epoxide **23** (Scheme 3) it gave the 1,2-diketone **28**.




**20** **21** 30% **22** 40%

A mechanism was later proposed (see Scheme 3) to account for the formation of the 1,2-diketone **28**. It was postulated that the isoaurone epoxide **23** was formed *in situ*, but underwent hydrolysis to give the carboxylic acid epoxide intermediate **24**. This epoxide intermediate **24** then underwent acid-catalysed hydrolysis to give the hemi-acetal **25** which was followed by loss of methanol to give the β-diketone **26**. The β–diketone **26** could then spontaneously decarboxylate to furnish the secondary alcohol **27**. Since secondary alcohols are easily oxidised to ketones using dimethyldioxirane,[3b] it appears likely that the secondary alcohol **27** was oxidised to the 1,2-diketone **28**, with the remainder of the dimethyldioxirane present in the reaction mixture.




Scheme 3

In conclusion, dimethyldioxirane can be useful in the selective synthesis of both chalcone epoxides and *trans*-2,3-dihydroflavonols, but of course, this depends on the type of β-arene group present in the substrate and on the pH of the reaction medium. We have also demonstrated an important advance in the synthesis of *trans*-2,3-dihydroflavonols, in that we can now obtain these compounds in far greater yield than previously.

## EXPERIMENTAL

*General.*—Melting points were determined on a Reichert-Jung Thermovar apparatus and are uncorrected. $^1$H NMR spectra were obtained using a Jeol JNM-PMX-60, a Jeol JNM-GX 270 FT, a Bruker AM-300 and a Varian Unity 300 spectrometer. $^{13}$C NMR were recorded on a Jeol JNM-GX 270 FT (67.80 MHz) spectrometer and such spectra were assigned using DEPT editing or by analogy with spectra obtained using such an editing technique. Tetramethylsilane was used as the internal standard in all NMR spectra recorded on the Jeol JNM-PMX-60 and the Jeol JNM-GX 270 FT spectrometer, and chemical shifts are reported as $\delta_H$(ppm) or $\delta_C$(ppm) from this standard. *J*-values are given in Hz. Infra-red spectra were recorded on a Perkin-Elmer 1710, a Perkin-Elmer 1740 Infra-red F.T. spectrometer, and a Mattison Galaxy Series F.T. I.R. 3000. Mass spectra were determined on a VG Analytical 70H and a Finnegan-Mat INCOS 50 mass spectrometer using electron impact and chemical ionization techniques. Elemental analyses were performed by the microanalytical department in the chemistry department at University College Dublin. Separations by column chromatography were performed using Merck Kieselgel 60 (Art. 7734). Merck precoated Kieselgel 60$F_{254}$ was used for TLC and Merck Kieselgel $PF_{254+336}$ for Preparative Layer Chromatography (PLC). All solvents were purified and dried by standard techniques.

(Z)-*2-Benzylidene-6-methoxybenzo[b]furan-3(2H)-one epoxide* **2**

(*Z*)-2-Benzylidene-6-methoxybenzo[b]furan-3(2H)-one **1** (0.113 g, 0.45 mmol) in anhydrous chloroform (5 mL) was treated with dimethyldioxirane (0.09 M in acetone; 6 mL) and stirred at room temperature under argon. Two more aliquots of dimethyldioxirane were added (2 x 2.5 mL ) over 34 h. Evaporation under reduced pressure gave a yellow oil, which crystallised from chloroform-petroleum spirits (b.p. 80-100°C) as cubes of (*Z*)-2-benzylidene-6-methoxybenzo[b]furan-3(2H)-one epoxide **2** (0.1 g, 83%), m.p. 103-104°C (lit.[10] m.p. 103°C); $\delta_H$ (270 MHz, $CDCl_3$) 3.86 (s, 6-OMe, 3H), 4.55 (s, β-H, 1H), 6.56 (d, *J* 2.2 Hz, 7-H, 1H), 6.71 (dd, *J* 8.8, 2.2 Hz, 5-H, 1H), 7.46 (m, Ph, 5H) and 7.63 (d, *J* 8.8 Hz, 4-H, 1H); $\delta_C$ (67.80 MHz, $CDCl_3$): 56.06 (6-OMe), 62.58 (β-C), 90.26 (2-C), 97.20 (7-C), 112.56 (5-C),113.19 (9-C), 125.72 (4-C), 127.51(2', 6'-C), 128.47 (4'-C), 129.09 (3', 5'-C), 131.95 (1'-C), 168.82 (8-C), 172.76 (6-C) and 189.51 (3-C); m/z 268 ($M^+$, 49), 251 ($M^+$-OH, 15), 240 ($M^+$-CO, 24), 175 ($M^+$ - $C_6H_5O$, 8), 134 ($M^+$ - OH - $C_8H_5O$, 46) and 106 ($M^+$ - CO - $C_8H_6O_2$ and/or $M^+$ -OH -$C_8H_5O$-CO, 37%) Note: $^{13}$C and mass spectra have not been shown previously.

(E)-*2-Benzylidene-6-methoxybenzo[b]furan-3(2H)-one epoxide* **4**

A mixture of (*E*)-2-benzylidene-6-methoxybenzo[b]furan-3(2H)-one **3** (0.076 g, 0.3 mmol) and dichloromethane (10 mL) was treated with dimethyldioxirane[20] (*ca.* 0.06 M in acetone; 17 mL) at 0°C. The reaction mixture was stirred at this temperature for 1 h before being allowed warm to room temperature and stirred for 36 h. The solvent was removed by evaporation under reduced pressure, to give a sticky solid (0.105 g), which consisted of (*E*)-2-benzylidene-6-methoxybenzo[b]furan-3(2H)-one epoxide **4** (33%) and (*E*)-2-benzylidene-6-methoxybenzo[b]furan-3(2H)-one **3** (67%), established by $^1$H nmr spectroscopy. For **4**; $\delta_H$ (270 MHz ; $CDCl_3$) 3.91 (s, 6-OMe, 3H), 4.74 (s, β-H, 1H), 6.60 (d, *J* 2.2 Hz, 7-H, 1H), 6.68 (dd, *J* 8.0, 2.2 Hz, 5-H, 1H), 7.39 (m, 3', 4', 5'-H, 3H), 7.51(d, *J* 8.0 Hz, 4-H, 1H) and 7.59 (dd, *J* 8.0, 2.2 Hz, 2', 6'-H, 2H); $\delta_C$ (67.80 MHz, $CDCl_3$) 56.06 (6-OMe), 64.38 (β-C), 88.52 (2-C), 96.77 (7-C), 111.99 (5-C), 114.13 (9-C), 125.56 (4-C), 127.25 (2', 6'-C), 127.92 (4'-C), 128.99 (3', 5'-C), 130.37 (1'-C), 168.63 (8-C), 171.47(6-C) and

188.25 (3-C); m/z 268 ($M^+$, 48), 252 (57), 251(100), 239 (23), 225 (13), 211(27), 151(27), 134 (24) and 118 (21%) Note: $^{13}C$ and mass spectra have not been shown previously.

(E)-*2'-Hydroxychalcone epoxide* **6**

A solution of (*E*)-2'-hydroxychalcone **5** (0.1 g, 0.45 mmol) in acetonitrile (31.5 mL) was treated with aqueous acetic acid (0.02 M; 12 mL) and aqueous sodium acetate (0.02 M; 3 mL). Dimethyldioxirane (0.073 M in acetone; 13.6 mL) was added at 0°C. The reaction mixture was allowed warm to room temperature and it was stirred at this temperature for *ca.* 25 h. The reaction mixture was diluted with diethyl ether (80 mL), washed with water (35 mL and 2 x 80 mL), dried ($CaSO_4$) and evaporation to dryness under reduced pressure furnished *trans*-2'-hydroxychalcone epoxide **6** (0.06 g, 60%) as an oil, which later solidified into prisms on standing, m.p. 66.5-70°C (lit.[11] m.p. 78°C); $\nu_{max}$ (KBr) 3035, 1645 and 1613 $cm^{-1}$; $\delta_H$ (270 MHz; $CDCl_3$) 4.12 (d, *J* 1.8 Hz, β-H, 1H), 4.34 (d, *J* 1.8 Hz, α-H, 1H), 6.90 (qd, *J* 8.0, 1.1 Hz, 5'-H, 1H), 7.03 (dd, *J* 8.6, 1.1 Hz, 3'-H, 1H),7.40 (m, β-Ph, 5H), 7.53 (qd, *J* 8.0, 1.5 Hz, 4'-H, 1H), 7.81 (dd, *J*8.0, 1.8 Hz, 6'-H, 1H), 11.90 (s, 2'-OH, 1H); $\delta_C$ (67.80 MHz; $CDCl_3$) 59.79 (β-C), 59.93 (α-C), 118.76 (3'-C), 118.81 (1'-C), 119.41 (5'-C), 125.80 (2, 6-C), 128.85 (4-C), 129.25 (3, 5-C), 129.41 (6'-C), 135.12 (1-C), 137.38 (4'-C), 163.00 (2'-C), 197.50 (C=O); m/z 240 ($M^+$, 13), 211 ($M^+$-CHO, 66), 133 ($M^+$-$C_7H_7O$, 60), 121 ($M^+$-$C_8H_7O$, 100), 91 ($C_7H_7^+$, 65%).

trans-2,3-*Dihydro-3-hydroxy-2-phenyl-4H-1-benzopyran-4-one* (trans-2,3-*Dihydroflavonol*) **7**

A solution of (*E*)-2'-hydroxychalcone **5** (0.063 g, 0.28 mmol) in dichloromethane (5 mL) was added to dimethyldioxirane (0.09 M in acetone; 3.5 mL) at 0°C. The temperature of the reaction mixture was gradually increased to room temperature over 14 h. After a further 24 h at room temperature an aliquot of dimethyldioxirane (0.1 M in acetone; 3 mL) was added at 0°C. The reaction mixture was allowed warm to room temperature over 43.5 h. The solvent was then removed by evaporation to afford a bright yellow solid (0.068 g). This was purified by PLC on silica gel developed with petroleum spirits (b.p. 60-80°C)—ethyl acetate (4 : 1) to give two bands listed in order of increasing polarity.

**Band 1:**

Afforded (*E*)-2'-hydroxychalcone **5** (0.003 g, 5%) as a yellow solid which crystallised from ethanol as yellow needles, m.p. 87-89°C (lit.[21] m.p 88-89°C).

**Band 2:**

Furnished *trans*-2,3-dihydro-3-hydroxy-2-phenyl-4H-1-benzopyran-4-one **7** (0.05 g, 74%) as a white crystalline solid, m.p. 177-178°C (lit.[15b] m.p. 178°C)(Found C, 74.88; H, 5.05 ; Calc. for $C_{15}H_{12}O_3$ C, 74.98; H, 5.04%.

(E)-*2'-Hydroxy-4-methoxychalcone epoxide* **9**

A solution of (*E*)-2'-hydroxy-4-methoxychalcone **8** (0.12 g, 0.47 mmol) in dichloromethane (5 mL) was treated with dimethyldioxirane (0.078 M in acetone; 7.3 mL) at 0°C under argon. The reaction mixture was stirred between 0°C and room temperature over a 25 h period. Evaporation of the solvent under reduced pressure, afforded *trans*-2'-hydroxy-4-methoxychalcone epoxide **9** (0.128 g, 100%) as a yellow semi-solid. (It remained in this state after crystallisation from chloroform-petroleum spirits (b.p. 60-80°C)); $\delta_H$ (60 MHz; $CDCl_3$) 3.84

(s, 4-OMe, 3H), 4.08 (d, *J* 2.4 Hz, β-H, 1H), 4.34 (d, *J* 2.4 Hz, α-H, 1H), 6.80-7.72 (m, 3', 4', 5'-H and β-Ph, 7H), 7.88 (dd, *J* 8.4, 2.0 Hz, 6'-H, 1H) and 11.92 (s, 2'-OH, 1H).

When this compound was heated in methanol, it furnished quantitatively *trans*-2,3-dihydro-3-hydroxy-2-(4-methoxyphenyl)-4H-1-benzopyran-4-one **10**, m.p. 167-169°C (lit.[15b] m.p. 168°C).

trans-2,3-*Dihydro-3-hydroxy-2-(4-methoxyphenyl)-4H-1-benzopyran-4-one* (trans-2,3-*Dihydro-4'-methoxyflavonol*) **10**

A solution of (*E*)-2'-hydroxy-4-methoxychalcone **8** (0.12 g, 0.47 mmol) in acetonitrile (31.5 mL) was treated with aqueous acetic acid (0.02 M; 12 mL) and aqueous sodium acetate (0.02 M; 3 mL). Dimethyldioxirane (0.073 M in acetone; 15 mL) was added at 0°C. After 20 h stirring between 0°C and room temperature, the reaction mixture was diluted with diethyl ether (80 mL), washed with water (4 x 60 mL), dried ($CaSO_4$) and evaporated to dryness to yield a pale yellow solid. Recrystallisation from ethanol gave *trans*-2,3-dihydro-3-hydroxy-2-(4-methoxyphenyl)-4H-1-benzopyran-4-one **10** (0.08 g, 62%) as needles, m.p. 168-170°C (lit.[15b] m.p. 168°C); $\delta_H$ (60 MHz; $CDCl_3$) 3.74 (s, 2-OH, 1H), 3.85 (s, 4'-OMe, 3H), 4.60 (d, *J* 12.0 Hz, 3-H, 1H), 5.12 (d, *J* 12.0 Hz, 2-H, 1H), 7.08 (m, 3', 5', 6, 7, 8-H, 5H), 7.52 (d, *J* 8.5 Hz, 2', 6'-H, 2H), 7.76 (dd, *J* 8.5, 2.5 Hz, 5-H, 1H); (Found C, 70.93; H, 5.44; calc. for $C_{16}H_{14}O_4$ C, 71.09; H, 5.23%).

*3-Hydroxy-2-phenyl-4H-1-benzopyran-4-one (flavonol)* **14**

Method A

A mixture of 2-phenyl-4H-1-benzopyran-4-one epoxide **12**[4] (0.1 g, 0.42 mmol) and methanol (10 mL) was stirred at room temperature for 8 h. Evaporation of the solvent yielded a yellow solid, which was recrystallised from ethanol to give needles of 3-hydroxy-2-phenyl-4H-1-benzopyran-4-one **14** (0.09 g, 90%), m.p. 166-168°C (lit.[11] m.p. 170°C). The $^1$H nmr spectrum was identical to that given in the literature.

Method B

A mixture of 2-phenyl-4H-1-benzopyran-4-one epoxide **12**[4] (0.23 g, 0.96 mmol), glacial acetic acid (15 mL) and acetone (5 mL) was stirred at room temperature for 42.5 h. The reaction was quenched by the addition of water (20 mL) this was followed by extraction with dichloromethane (40 mL), drying ($CaSO_4$) and evaporation to a quarter the original volume to give a yellow precipitate. This was filtered, washed with water and dried to give 3-hydroxy-2-phenyl-4H-1-benzopyran-4-one **14** (0.15 g, 64%) as yellow needles, m.p. 167-169°C (lit.[11] m.p. 170°C). This solid gave a positive ferric chloride reaction; (Found C, 75.87; H, 4.58; calc. for $C_{15}H_{10}O_3$ C, 75.61; H, 4.31%.). The $^1$H nmr spectrum was identical to that given in the literature.

*2-Benzoyl-2-hydroxybenzo[b]furan-3(2H)-one* **16**

A mixture of 3-hydroxy-2-phenyl-4H-1-benzopyran-4-one **14** (0.2 g, 0.84 mmol) and dichloromethane (7 mL) was treated with dimethyldioxirane (0.118 M in acetone; 11 mL) at 0°C under argon. Stirring was continued at 0°C for 2.3 h and this was followed by stirring at room temperature for 25 h. The solvent was removed by evaporation under reduced pressure to give a pale yellow oil, which solidified later. Recrystallisation from chloroform—petroleum spirits (b.p. 60-80°C) furnished 2-benzoyl-2-hydroxybenzo[b]furan-3(2H)-one **16** (0.12 g, 56%) as pale yellow needles, m.p. 93-95°C (lit.[17a] m.p. 95-97°C). This compound gave a positive ferric chloride reaction; $\nu_{max}$ (KBr) 3308, 1709 and 1611 cm$^{-1}$; $\delta_H$ (60 MHz; $CDCl_3$) 7.15-7.82 (m, 4, 5, 6, 7-H and COPh); $\delta_C$ (67.80 MHz; $CDCl_3$) 114.14 (7-C), 119.09 (2-C), 123.60 (5-C), 124.08 (9-C), 125.78 (4-C),

129.00 (3', 5'-C), 129.44 (2', 6'-C), 131.38 (1'-C), 135.02 (4'-C), 139.42 (6-C), 171.25 (8-C), 190.88 (*C*OPh), 195.16 (3-C); m/z 254 ($M^+$, 7), 238 ($M^+$-O, 5), 133 ($M^+$-$C_7H_5O_2$, 2), 122 ($M^+$-$C_8H_4O_2$, 40), 105 ($M^+$-$C_8H_4O_2$, 40), 105 ($M^+$-$C_8H_5O_3$, 100), 77 ($C_6H_5^+$, 46%); (Found C, 70.79; H, 4.03; calc. for $C_{15}H_{10}O_4$ C, 70.86; H, 3.97%.) .

*1-(2-hydroxy-4-methoxyphenyl)-2-phenylethandione* **28**

A mixture of (*E*)-3-(α-methoxybenzylidene)-6-methoxybenzo[b]furan-2(3H)-one **21**[18] (0.073 g, 0.26 mmol) and dichloromethane (5 mL) was treated with dimethyldioxirane (0.118 M in acetone; 4.5 mL) at 0°C under argon. The reaction was stirred at 0°C for 2.3 h, then it was warmed to room temperature and stirred for 25 h. Evaporation to dryness under reduced pressure afforded a yellow oil, which was purified by PLC on silica gel developed with petroleum spirits (b.p. 60-80°C)—ethyl acetate (7:3) to give 1-(2-hydroxy-4-methoxyphenyl)-2-phenylethandione **28** (0.022 g, 33%) as a yellow solid, which crystallised as needles from ethanol-water, m.p. 91-92°C (lit.[22] m.p. 86-87°C). This solid gave a positive ferric chloride reaction; $\nu_{max}$ (KBr) 1715, 1681 and 1621 $cm^{-1}$; $\delta_H$ (270 MHz ; $CDCl_3$) 3.87 (s, 4'-OMe, 3H), 6.43 (dd, *J* 9.0, 2.5 Hz, 5'-H, 1H), 6.52 (d, *J* 2.5 Hz, 3'-H, 1H), 7.83 (d, *J* 9.0 Hz, 6'-H, 1H), 7.52 (t, *J* 8.0, 1.4 Hz, 3", 5"-H, 2H), 7.67 (td, *J* 8.0, 1.4 Hz, 4"-H, 1H), 7.99 (dd, *J* 8.0, 1.4 Hz, 2", 6"-H, 2H) and 11.89 (s, 2'-OH, 1H); $\delta_C$ (67.80 MHz ; $CDCl_3$) 55.82 (4'-$OCH_3$), 101.20 (3'-C), 108.91 (5'-C), 111.07 (1'-C), 129.07 (3", 5"-C), 130.07 (2", 6"-C), 132.93 (1"-C), 133.98 (6'-C), 135.02 (4"-C), 166.59 (2'-C), 167.67 (4'-C), 192.16 (1-C) and 196.90 (2-C); m/z 256 ($M^+$, 5), 227 ($M^+$-CHO, 3), 151($M^+$-$C_7H_5O$, 100), 123 ($M^+$-$C_8H_5O_2$, 2), 105 ($C_7H_5O^+$, 37) and 95 ($M^+$-$C_9H_5O_3$, 17%); (Found C, 70.56; H, 4.64; calc. for $C_{15}H_{12}O_4$ C, 70.29; H, 4.72%) (Found $M^+$, 256.0746. $C_{15}H_{12}O_4$ requires M, 256.0732).

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