Epoxidation of Flavones by Dimethyldioxirane

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The synthesis of epoxides **2** by epoxidation of flavones **1** with isolated dimethyldioxirane (as acetone solution) at subambient temperatures is reported. These labile epoxides were isolated and completely characterized by UV, IR, ^{1}H and ^{13}C NMR, MS, and C, H analyses. Warming to room temperature led to rearrangement to afford quantitatively the 3-hydroxyflavones **3b,h,i,n**. Treatment of the epoxides **2b,f** with methanol led to the 3-hydroxy-2-methoxyflavanones **4b,f** as a mixture of cis and trans isomers.

Introduction

Flavones and their regioisomers isoflavones are common natural products which are widely distributed among many plants;[2] they provide the color (from pale yellow to orange) in flowers, trees, and fruits. Furthermore, the flavone molecule contains a C=C bond which bears the electron-accepting oxo and the electron-donating alkoxy group in such a way that conjugation results in a unreactive substrate toward electrophilic as well as nucleophilic epoxiding agents. While isoflavone epoxides have been prepared[3] by the alkaline H_2O_2 epoxidation of isoflavones (Weitz-Scheffer reaction), no example of flavone epoxides appear to be known, compounds which should serve as potentially useful intermediates for synthetic purposes in flavone chemistry. Thus, attempts to convert flavones to their epoxides by the classical oxidants[4] like alkaline H_2O_2 and *m*-CPBA have failed and phenyl iodosyl diacetate, PhI(OAc)$_2$,[5] yielded 3-hydroxyflavones, presumably by rearrangement of the intermediary epoxides. Oxidants like $KMnO_4$,[6] NiO_2,[7] SeO_2,[8] and Tl(OAc)$_3$[9] proved to be inert toward the flavone moiety.

It can be easily recognized that a successful epoxidation of flavones requires an oxidant which is efficient in transferring an oxygen atom, mild toward the oxidized product, and performs under strictly neutral conditions. Dimethyldioxirane[10] (as acetone solution[11]) is a powerful and selective oxidant which had been proven as the reagent of choice for the epoxidation of electron-rich alkenes such as enol ethers,[12] silyl enol ethers,[13] enol phosphates,[14] γ-methylene-γ-butyrolactones,[15] benzo[*b*]furans,[16] enol esters and lactones,[17] vinyl formamides,[18] and vinyl carbamates[19] as well as electron-poor alkenes such as α,β-unsaturated acids, esters and ketones,[20] and β-oxo enol ethers.[21] For the latter cases, which possess the same functional group as flavones, elevated temperatures (up to 30 °C), extended reaction times (up to 2 d), and excess of dioxirane (up to 3 equiv) were necessary for the complete conversion of these sluggish substrates.

Indeed, we report[22] here that a variety of flavones **1** were converted at subambient temperatures to their hitherto unknown epoxides **2** by isolated dimethyldioxirane in ex-

Scheme I

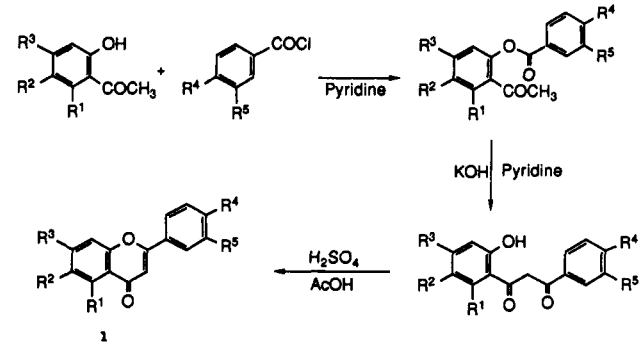

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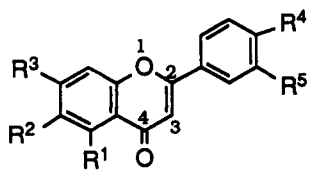
Table I. Epoxidation[a] of Flavones by Dimethyldioxirane (DMD)[b]

	substituents						reaction cond	
flavone	R^1	R^2	R^3	R^4	R^5	ratio 1:DMD	temp (°C)	time (h)
1a	H	H	H	H	H	1:6	0	36
1b	H	H	H	CH_3	H	1:4	0	23
1c	H	H	H	CH_3O	H	1:3	0	24
1d	H	H	H	NO_2	H	1:7	ca. 20	72
1e	H	H	H	Cl	H	1:6	0	61[c]
1f	H	H	H	H	Cl	1:6	ca. 20	28
1g	H	CH_3	H	H	H	1:4	0	41
1h	H	CH_3	H	CH_3	H	1:3	−10	34
1i	H	CH_3	H	CH_3O	H	1:4	0	23
1j	H	CH_3	H	Cl	H	1:4	ca. 20	27
1k	H	CH_3	H	H	Cl	1:4	ca. 20	37
1l	CH_3O	H	H	H	H	1:4	0	26
1m	H	CH_3O	H	H	H	1:7	−10	48
1n	H	H	CH_3O	H	H	1:5	−10	46

[a] In CH_2Cl_2/CH_3COCH_3 at −10 °C to room temperature (ca. 20 °C) under N_2 atmosphere; ca. 100% yield of isolated pure product **2** at complete conversion of **1**. [b] 0.060–0.098 M in acetone. [c] 92% conversion.

Table II. Selected Spectral Data of Flavones 1a–n and Epoxides 2a–n



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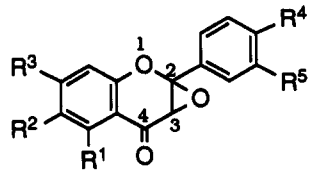

2

			δ(¹³C)						δ(¹³C)		
flavone	IR[a] ν_{CO} (cm^{-1})	δ(¹H)[b] 3-H	C-2	C-3	C-4	epoxide	IR[a] ν_{CO} (cm^{-1})	δ(¹H)[b] 3-H	C-2	C-3	C-4
1a	1650	6.83	163.4	107.6	178.4	**2a**	1715	3.84	84.9	63.8	188.2
1b	1650	6.77	163.5	106.9	178.4	**2b**	1685	4.00	86.0	64.1	188.5
1c	1650	6.74	163.4	106.2	178.4	**2c**	1695	3.75	85.6	64.0	187.9
1d	1670	6.93	160.6	109.6	178.0	**2d**	1725	3.94	84.4	64.0	187.6
1e	1645	6.78	162.2	107.6	178.2	**2e**	1695	3.85	84.5	63.8	188.1
1f	1655	6.72	161.5	108.0	177.9	**2f**	1710	3.86	84.3	63.8	188.0
1g	1665	6.78	163.0	107.2	178.4	**2g**	1710	3.83	85.3	64.2	188.8
1h	1660	6.64	163.2	106.6	178.4	**2h**	1690	3.91	85.3	64.4	188.8
1i	1655	6.68	163.2	106.0	178.4	**2i**	1700	3.84	85.4	64.4	188.9
1j	1675	6.72	161.9	107.4	178.2	**2j**	1725	3.81	84.4	63.8	188.2
1k	1660	6.75	161.5	107.9	178.2	**2k**	1700	3.82	84.0	63.6	187.9
1l	1665	6.82	161.0	106.4	178.3	**2l**	1705	3.86	84.1	65.7	187.7
1m	1650	6.81	163.1	106.8	178.3	**2m**	1695	3.86	84.7	63.6	188.0
1n	1655	6.67	162.7	107.2	177.5	**2n**	1685	3.94	86.1	63.5	186.8

[a] In CCl_4 (Perkin-Elmer 1420 instrument). [b] In $CDCl_3$ (Bruker AC 250 (250 MHz)) except **2b** in CD_3COCD_3 (Bruker AC 200 (200 MHz)), except **2c** in C_6D_6 (Bruker AC 200 (200 MHz)), except **2g,h** in CD_2Cl_2 (Bruker AC 200 (200 MHz)).

cellents yields (>95%). For the first time these labile epoxides have been made available for synthetic chemistry.

Results and Discussion

Flavone **1a** was commercially available, while the known flavones **1b–n** were prepared in moderate overall yields according to the known three-step sequence[23] shown in Scheme I. For this purpose, the 2-(aroyloxy)acetophenones were obtained from the reaction of the substituted 2-hydroxyacetophenones with the corresponding aroyl chlorides. Their rearrangement into 2-hydroxydiaroylmethane was achieved upon treatment with hot pulverized 85% potassium hydroxide by heating in pyridine. Finally, cyclization of the resulting diketone with concd sulfuric acid in glacial acetic acid afforded the desired flavones **1**. The unknown flavone **1k** was also prepared analogous to this sequence (Scheme I).

The flavones **1a–n** were transformed with the help of isolated dioxirane (as acetone solution) into the corresponding epoxides **2a–n** (Scheme II) in quantative yields. The detailed oxidation conditions are given in Table I. In view of the reduced reactivity of these π-systems, long reaction times (23–72 h), elevated temperatures (up to 20 °C), and a large excess of dioxirane (up to 7 equiv) were necessary for achieving complete conversion of the flavones **1** into the corresponding epoxides **2**. It was advantageous to administer the dioxirane in batches in ca. 12-h intervals.

Besides satisfactory elemental analyses for these hitherto unknown epoxides **2**, their characterization rests on spectral data which include IR, ¹H and ¹³C NMR, and MS. The pertinent characteristic data are given in Table II. In their IR spectra all epoxides **2** exhibit the expected shift of the carbonyl stretching band to 1685–1725 cm^{-1} from 1645–1670 cm^{-1} in the flavones **1**. The epoxide proton signals occur at δ = 3.84–4.00, the expected upfield shift from δ = 6.64–6.93 for the olefinic proton signal of flavones **1**. In the ¹³C NMR spectra the C-2, C-3, and C-4 carbon atoms in the epoxides **2** are located at δ = 84.0–86.2, 63.5–65.9, and 186.8–188.9 versus δ = 160.6–163.5, 106.0–109.6, and 177.7–178.4 for the flavones **1** and are particularly diagnostic for the structure of the epoxides

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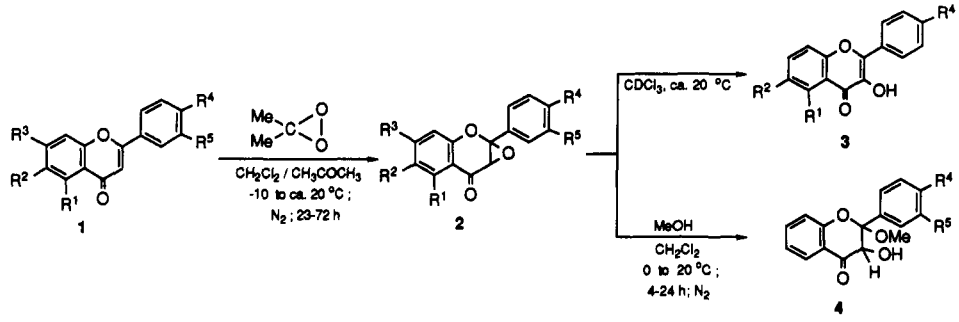
Scheme II



2. Futhermore, molecular ions were observed in the mass spectra.

The flavone epoxides **2** are thermally labile compounds, especially when they bear electron-donating substituents at the 4′-position. On standing at room temperature for some hours, they rearrange into the corresponding 3-hydroxyflavones **3** (Scheme II). More effectively, epoxide **2b** was converted within minutes at 0 °C quantitatively into 3-hydroxy-4′-methylflavone (**3b**) on treatment with catalytic amounts of *p*-toluenesulfonic acid, while several days at 20 °C are necessary without acid. This shows once again the advantage of dimethyldioxirane as oxidant, which oxidizes under strictly neutral conditions, otherwise it would have been difficult to isolate these epoxides.

The propensity of the flavone epoxides **2** toward solvolysis is demonstrated in their ease of reaction with methanol. As examples, the methanolysis of the epoxides **2b,f** were investigated. Thus, epoxide **2b** reacted with methanol at 0 °C to give quantitatively the 3-hydroxy-2-methoxy-4′-methylflavone (**4b**) as a mixture of cis and trans isomers (Scheme II). The more persistent epoxide **2f** gave the 3′-chloro-3-hydroxy-2-methoxyflavone (**4f**) only slowly with methanol even at ca. 20 °C.

In summary, the by now well-known[10] oxygen transfer agent dimethyldioxirane converts flavones **1** efficiently into their corresponding, hitherto unknown epoxides **2**. These thermally labile epoxides rearrange on standing already at room temperature (ca. 20 °C) into hydroxyflavones **3**, a rearrangement that is readily catalyzed by acids. The convenience of preparation of these novel epoxides and their ease of reaction with protic nucleophiles, here demonstrated for methanol, should open up new perspectives in flavone chemistry.

Experimental Section

Instrumentation and Materials. Melting points were determined on a Reichert Thermovar hot-stage apparatus. The UV spectra were measured on a Hitachi U-3200 spectrophotometer. The IR spectra were recorded on a Perkin-Elmer 1420 instrument. ^1H and ^{13}C NMR spectra were run on a Bruker AC 200 (200-MHz) or a Bruker AC 250 (250-MHz) spectrometer, chemical shifts refer to chloroform-*d*, methylene chloride-d_2, or acetone-d_6. Except when otherwise stated, all NMR measurements were conducted at room temperature (ca. 20 °C). Mass spectra were obtained on a Varian Finnigan MAT 8200. Elemental analyses were performed in-house. All solvents were purified by following standard literature methods. Acetone and water, used in the preparation of dimethyldioxirane, were doubly distilled over EDTA. Caroate (potassium monoperoxosulfate), the triple salt $2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$, was used as received. *Dimethyldioxirane* (as acetone solution) was prepared according to the published procedure,[11a] and its peroxide content was determined by oxidation of methyl phenyl sulfide, the latter quantitated by ^1H NMR. The dimethyldioxirane solutions were stored over molecular sieves (4 Å) at −20 °C.

Preparation of 6-Methyl-3′-chloroflavone (1k). The flavone **1k** (5.98 g, 45%) was obtained as colorless needles, mp 132 °C (from EtOH), according to the sequence in Scheme I, by starting from 7.65 g (49.6 mmol) of 2-hydroxy-5-methylacetophenone and 13.1 g (74.9 mmol) of 3-chlorobenzoyl chloride. IR (CCl_4): ν = 3080 (w), 3040 (w), 2930 (w), 1660 (s), 1620 (m), 1585 (m), 1570 (m), 1490 (m), 1440 (m), 1360 (s), 1290 (m), 1255 (w), 1230 (m), 1140 (m), 1105 (w), 1085 (m), 1045 (m), 930 (w), 855 (m), 700 (m) cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ = 2.45 (s, 3 H), 6.75 (s, 1 H), 7.40–7.53 (m, 4 H), 7.73–7.77 (m, 1 H), 7.87–7.89 (m, 1 H), 7.98–7.99 (m, 1 H). ^{13}C NMR (63 MHz, $CDCl_3$): δ = 20.9 (q), 107.9 (d), 117.8 (d), 123.5 (s), 124.3 (d), 125.1 (d), 126.3 (d), 130.3 (d), 131.4 (d), 133.7 (s), 135.2 (s), 135.4 (d), 154.0 (s), 161.5 (s), 178.2 (s). MS (70 eV): *m/z* (rel. abund.) = 272 (27, $M^+ + 2$), 270 (77, M^+), 244 (6, $M^+ - C_2H_2$), 242 (18, $M^+ - CO$), 134 (100, $M^+ - C_8H_5Cl$), 121 (10, $M^+ - C_9H_6Cl$), 106 (15, $M^+ - C_8H_5ClO$), 105 (12, $M^+ - C_9H_6ClO$), 89 (16, $M^+ - C_9H_6ClO_2$), 76 (15, $M^+ - C_{10}H_7ClO_2$). Anal. Calcd for $C_{16}H_{11}ClO_2$ (270.7): C, 70.99; H, 4.10. Found: C, 71.26; H, 4.06.

Epoxidation of Flavones 1a–n by Dimethyldioxirane (as Acetone Solution). General Procedure. The required amount of the dioxirane in acetone (0.050–0.098 M), which was dried over molecular sieves (4 Å) at −20 °C, was added rapidly under N_2 to a cooled solution (cf. Table I) of the flavones **1a–n** (0.069–1.140 mmol) in absolute CH_2Cl_2 (10 mL). The stirring was continued for 12 h, and a new quantity of the dioxirane solution was rapidly added and stirred for 12 h. The addition of dioxirane was continued in 12-h intervals until complete consumption (TLC) of the flavone. The solvent was removed under vacuum (0 to ca. 20 °C (15 Torr)) to yield the hitherto unknown epoxides **2a–n** in analytical purity and in excellent yields (≥90%).

1a,7a-Dihydro-1a-phenyl-7*H*-oxireno[*b*][1]benzopyran-7-one (2a). 200 mg (ca. 100%) was obtained as colorless needles, mp 99–100 °C (from $CHCl_3$/petroleum ether) by following the above procedure at 0 °C for 36 h, in which a total of 61.5 mL of 0.084 M (5.14 mmol) dioxirane and 187 mg (0.840 mmol) of flavone (**1a**) were employed. UV (CH_2Cl_2): λ_{max} (log ϵ) = 225.6 (4.486), 254.4 (4.470), 311.8 (4.099) nm. IR (CCl_4): ν = 3060 (w), 3000 (w), 1715 (s), 1635 (m), 1490 (w), 1480 (s), 1420 (w), 1345 (m), 1340 (s), 1280 (w), 1230 (s), 1120 (m), 1015 (m), 950 (m), 920 (w), 705 (m), 680 (w) cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ = 3.84 (s, 1 H), 7.14–7.20 (m, 2 H), 7.41–7.47 (m, 3 H), 7.54–7.64 (m, 3 H), 7.92–7.96 (m, 1 H). ^{13}C NMR (63 MHz, $CDCl_3$): δ = 63.8 (d), 84.9 (s), 118.2 (d), 119.3 (s), 123.4 (d), 125.9 (d), 127.1 (d), 128.7 (d), 129.9 (d), 132.9 (s), 136.2 (d), 156.2 (s), 188.3 (s). MS (70 eV): *m/z* (rel. abund.) = 238 (22, M^+), 211 (9, $M^+ - C_2H_3$), 210 (63, $M^+ - CO$), 209 (88, $M^+ - CHO$), 181 (29, $M^+ - C_2HO_2$), 152 (9, $M^+ - C_3H_2O_3$), 106 (7, $M^+ - C_8H_4O_2$), 105 (100, $M^+ - C_8H_5O_2$), 77(80, $M^+ - C_9H_5O_3$), 76 (15, $M^+ - C_9H_6O_3$). Anal. Calcd for $C_{15}H_{10}O_3$ (238.3): C, 75.62; H, 4.23. Found: C, 75.89; H, 4.20.

1a,7a-Dihydro-1a-(4-methylphenyl)-7*H*-oxireno[*b*][1]-benzopyran-7-one (2b). 228 mg (ca. 100%) was obtained as a colorless powder, mp 101–103 °C (from CCl_4/petroleum ether) by following the above procedure at 0 °C for 23 h, in which a total of 50 mL of 0.068 M (3.38 mmol) dioxirane and 213 mg (0.900 mmol) of 4′-methylflavone (**1b**) was employed. IR (CCl_4): ν = 1685 (s), 1610 (w), 1475 (m), 1460 (s), 1410 (w), 1325 (m), 1215 (m), 1180 (m), 1120 (w), 1105 (m), 1005 (m), 990 (m), 970 (s), 940 (m), 940 (m), 625 (w) cm^{-1}. ^1H NMR (200 MHz, CD_3COCD_3): δ = 2.38 (s, 3 H), 4.00 (s, 1 H), 7.24–7.34 (m, 4 H), 7.58 (d, J = 8.18 Hz, 2 H), 7.68–7.75 (m, 1 H), 7.93 (dd, J_1 = 8.01 Hz, J_2 = 1.67 Hz, 1 H). ^{13}C NMR (50 MHz, CD_3COCD_3): δ = 21.2 (q), 64.1 (d), 86.0 (s), 119.0 (d), 120.0 (s), 124.2 (d), 126.6 (d), 127.5

(d), 130.1 (d), 131.3 (s), 137.1 (s), 140.7 (s), 157.1 (s), 188.5 (s). MS (70 eV): m/z (rel. abund.) = 252 (44, M^+), 251 (27, $M^+ - H$), 237 (14, $M^+ - CH_3$), 224 (70, $M^+ - CO$), 223 (100, $M^+ - CHO$), 209 (13, $M^+ - C_2H_3O$), 195 (28, $M^+ - C_3H_5O$), 181 (24, $M^+ - C_4H_7O$), 165 (16, $M^+ - C_4H_7O_2$), 152 (22, $M^+ - C_5H_8O_2$), 119 (88, $M^+ - C_8H_5O_2$), 91 (87, $M^+ - C_9H_5O_3$), 77 (19, $M^+ - C_{10}H_7O_3$), 76 (22, $M^+ - C_{10}H_8O_3$). Anal. Calcd for $C_{16}H_{12}O_3$ (252.3): C, 76.18; H, 4.79. Found: C, 76.41; H, 4.81.

1a,7a-Dihydro-1a-(4-methoxyphenyl)-7*H*-oxireno[*b*][1]benzopyran-7-one (2c). 306 mg (ca. 100%) was obtained as a colorless powder, mp 94–96 °C (from CCl_4/petroleum ether), by following the above procedure at 0 °C for 24 h, in which a total of 50 mL of 0.068 M (3.38 mmol) dioxirane and 288 mg (1.14 mmol) of 4′-methoxyflavone (**1c**) was employed. UV (CH_2Cl_2): λ_{max} (log ϵ) = 226.8 (4.328), 254.8 (4.180), 313.2 (3.761) nm. IR (CCl_4): ν = 2980 (w), 1695 (s), 1615 (m), 1580 (w), 1510 (m), 1455 (s), 1320 (m), 1300 (w), 1250 (s), 1205 (m), 1170 (m), 1150 (w), 1115 (m), 1105 (w), 1000 (m), 985 (s), 965 (s), 935 (w), 625 (w) cm^{-1}. ^1H NMR (200 MHz, C_6D_6): δ = 3.40 (s, 3 H), 3.75 (s, 1 H), 6.77–6.88 (m, 3 H), 6.96 (dd, J_1 = 8.38 Hz, J_2 = 1.05 Hz, 1 H), 7.09–7.17 (m, 1 H), 7.42–7.50 (m, 2 H), 8.07 (dd, J_1 = 7.82 Hz, J_2 = 1.65 Hz, 1 H). ^{13}C NMR (50 MHz, C_6D_6): δ = 54.9 (q), 64.0 (d), 85.6 (s), 114.3 (d), 118.2 (d), 119.9 (s), 123.3 (d), 123.5 (s), 127.3 (d), 127.7 (d), 135.9 (d), 156.6 (s), 161.2 (s), 187.9 (s). MS (70 eV): m/z (rel. abund.) = 268 (83, M^+), 153 (18, $M^+ - CH_3$), 240 (56, $M^+ - CO$), 239 (100, $M^+ - CHO$), 225 (19, $M^+ - C_2H_3O$), 211 (27, $M^+ - C_3H_5O$), 197 (23, $M^+ - C_4H_7O$), 181 (14, $M^+ - C_4H_7O_2$), 168 (11, $M^+ - C_5H_8O_2$), 135 (53, $M^+ - C_8H_5O_3$), 107 (16, $M^+ - C_9H_5O_3$), 77 (40, $M^+ - C_{10}H_7O_4$), 76 (18, $M^+ - C_{10}H_8O_4$). Anal. Calcd for $C_{16}H_{12}O_4$ (268.3): C, 71.64; H, 4.51. Found: C, 71.09; H, 4.50.

1a,7a-Dihydro-1a-(4-nitrophenyl)-7*H*-oxireno[*b*][1]benzopyran-7-one (2d). 224 mg (ca. 100%) was obtained as a colorless powder, mp 149–150 °C (from $CHCl_3$/petroleum ether), by following the above procedure at ca. 20 °C for 72 h, in which a total of 60 mL of 0.098 M (5.86 mmol) dioxirane and 211 mg (0.790 mmol) of 4′-nitroflavone (**1d**) was employed. UV (CH_2Cl_2): λ_{max} (log ϵ) = 262.4 (4.430) nm. IR (CCl_4): ν = 1725 (s), 1635 (m), 1560 (s), 1485 (m), 1370 (m), 1345 (m), 1340 (m), 1230 (m), 1135 (m), 1120 (w), 1020 (w), 945 (w), 870 (m) cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ = 3.94 (s, 1 H), 7.23–7.32 (m, 2 H), 7.65–7.72 (m, 1 H), 7.83 and 8.33 (AA′BB′ system, 4 H), 7.93–7.98 (m, 1 H). ^{13}C NMR (63 MHz, $CDCl_3$): δ = 64.0 (d), 84.4 (s), 118.5 (d), 119.5 (s), 124.2 (d), 124.3 (d), 127.4 (d), 127.5 (d), 137.0 (d), 140.0 (s), 149.2 (s), 156.1 (s), 187.6 (s). MS (70 eV): m/z (rel. abund.) = 283 (25, M^+), 256 (18, $M^+ - C_2H_3$), 255 (100, $M^+ - CO$), 254 (73, $M^+ - CHO$), 209 (18, $M^+ - CNO_3$), 208 (28, $M^+ - CHNO_3$), 196 (29, $M^+ - C_2HNO_3$), 150 (72, $M^+ - C_8H_4O_2$), 120 (28, $M^+ - C_8H_5NO_3$), 105 (16, $M^+ - C_8H_4NO_4$), 104 (67, $M^+ - C_8H_5NO_4$), 92 (22, $M^+ - C_9H_5NO_4$), 76 (63, $M^+ - C_9H_5NO_5$). Anal. Calcd for $C_{15}H_9NO_5$ (283.3): C, 63.61; H, 3.20; N, 4.95. Found: C, 63.81; H, 3.18; N, 4.93.

1a,7a-Dihydro-1a-(4-chlorophenyl)-7*H*-oxireno[*b*][1]benzopyran-7-one (2e). 216 mg (ca. 100% at 92% conversion) was obtained as a colorless powder, mp 149–150 °C (from $CHCl_3$/petroleum ether), by following the above procedure at 0 °C for 61 h, in which a total of 75 mL of 0.068 M (5.07 mmol) dioxirane and 221 mg (0.860 mmol) of 4′-chloroflavone (**1e**) was employed. IR (CCl_4): ν = 1695 (s), 1615 (m), 1500 (w), 1480 (w), 1465 (s), 1415 (w), 1330 (s), 1325 (s), 1270 (w), 1215 (m), 1155 (w), 1120 (s), 1110 (m), 1100 (m), 1095 (m), 1010 (m), 930 (m), 610 (m) cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ = 3.85 (s, 1 H), 7.18–7.22 (m, 2 H), 7.46 and 7.57 (AA′BB′ system, 4 H), 7.60–7.67 (m, 1 H), 7.97 (dd, J_1 = 7.86 Hz, J_2 = 1.67 Hz, 1 H). ^{13}C NMR (63 MHz, $CDCl_3$): δ = 63.8 (d), 84.5 (s), 118.2 (s), 119.3 (s), 123.6 (d), 127.3 (d), 127.4 (d), 129.1 (d), 131.6 (s), 136.2 (s), 136.4 (d), 156.1 (s), 188.1 (s). MS (70 eV): m/z (rel. abund.) = 274 (9, $M^+ + 2$), 272 (27, M^+), 256 (9, $M^+ - O$), 245 (36, $M^+ - C_2H_3$), 244 (53, $M^+ - CO$), 243 (89, $M^+ - CHO$), 209 (40, $M^+ - CClO$), 181 (9, $M^+ - C_3H_4ClO$), 152 (14, $M^+ - C_4H_5ClO_2$), 141 (100, $M^+ - C_8H_3O_2$), 111 (60, $M^+ - C_9H_5O_3$). Anal. Calcd for $C_{15}H_9ClO_3$ (272.7): C, 66.07; H, 3.33. Found: C, 66.52; H, 3.19.

1a,7a-Dihydro-1a-(3-chlorophenyl)-7*H*-oxireno[*b*][1]benzopyran-7-one (2f). 212 mg (ca. 100%) was obtained as colorless needles, mp 115–116 °C (from $CHCl_3$)/petroleum ether) by following the above procedure at ca. 20 °C for 28 h, in which a total of 55 mL of 0.084 M (4.63 mmol) dioxirane and 200 mg (0.780 mmol) of 3′-chloroflavone (**1f**) was employed. IR (CCl_4): ν = 1710 (s), 1625 (m), 1595 (w), 1490 (w), 1475 (s), 1425 (w), 1330 (m), 1270 (m), 1225 (m), 1160 (w), 1140 (m), 1085 (m), 1040 (w), 950 (w), 695 (w) cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ = 3.86 (s, 1 H), 7.19–7.27 (m, 2 H), 7.39–7.52 (m, 3 H), 7.61–7.67 (m, 2 H), 7.97 (dd, J_1 = 7.87 Hz, J_2 = 1.64 Hz, 1 H). ^{13}C NMR (63 MHz, $CDCl_3$): δ = 63.8 (d), 84.3 (s), 118.2 (d), 119.3 (s), 123.7 (d), 124.1 (d), 126.4 (d), 127.3 (d), 130.1 (d), 130.2 (d), 134.9 (s), 136.4 (d), 156.1 (s), 188.0 (s). MS (70 eV): m/z (rel. abund.) = 274 (7, $M^+ + 2$), 272 (19, M^+), 245 (35, $M^+ - C_2H_3$), 244 (71, $M^+ - CO$), 243 (77, $M^+ - CHO$), 209 (33, M^+ CClO), 208 (42, $M^+ - CHClO$), 181 (12, $M^+ - C_3H_4ClO$), 152 (15, $M^+ - C_4H_5ClO_2$), 141 (32, $M^+ - C_8H_3O_2$), 139 (100, $M^+ - C_8H_5O_2$), 111 (60, $M^+ - C_9H_5O_3$), 76 (32, $M^+ - C_9H_5ClO_3$), 75 (33, $M^+ - C_9H_6ClO_3$). Anal. Calcd for $C_{15}H_9ClO_3$ (272.7): C, 66.07; H, 3.33. Found: C, 65.92; H, 3.27.

1a,7a-Dihydro-5-methyl-1a-phenyl-7*H*-oxireno[*b*][1]benzopyran-7-one (2g). 233 mg (ca. 100%) was obtained as a colorless powder, mp 104–105 °C (from $CHCl_3$/petroleum ether) by following the above procedure at 0 °C for 41 h, in which a total of 60 mL of 0.068 M (4.05 mmol) dioxirane and 218 mg (0.923 mmol) of 6-methylflavone (**1g**) was employed. IR (CCl_4): ν = 3100 (w), 3060 (w), 2980 (w), 2940 (w), 1710 (s), 1640 (m), 1600 (w), 1510 (s), 1465 (m), 1440 (m), 1330 (m), 1320 (s), 1285 (w), 1240 (s), 1190 (w), 1150 (m), 1130 (m), 1085 (m), 1025 (m), 955 (m), 930 (m), 910 (w), 890 (w), 710 (m) cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ = 2.33 (s, 3 H), 3.83 (s, 1 H), 7.08 (d, J = 8.49 Hz, 1 H), 7.38–7.47 (m, 4 H), 7.56–7.63 (m, 2 H), 7.70 (d, J = 1.57 Hz, 1 H). ^{13}C NMR (63 MHz, $CDCl_3$): δ = 20.7 (q), 64.2 (d), 85.3 (s), 118.4 (d), 119.4 (s), 126.4 (d), 127.0 (d), 129.2 (d), 130.4 (d), 133.6 (s), 133.7 (s), 137.8 (d), 154.8 (s), 188.8 (s). MS (70 eV): m/z (rel. abund.) = 252 (16, M^+), 224 (36, $M^+ - CO$), 223 (53, $M^+ - CHO$), 195 (11, $M^+ - C_2HO$), 165 (4, $M^+ - C_3H_3O_2$), 152 (4, $M^+ - C_4H_4O_2$), 129 (3, $M^+ - C_7H_7O_2$), 105 (100, $M^+ - C_9H_7O_2$), 77 (59, $M^+ - C_{10}H_7O_3$), 76 (3, $M^+ - C_{10}H_7O_3$). Anal. Calcd for $C_{16}H_{12}O_3$ (252.6): C, 76.18; H, 4.79. Found: C, 76.18; H, 4.73.

1a,7a-Dihydro-5-methyl-1a-(4-methylphenyl)-7*H*-oxireno[*b*][1]benzopyran-7-one (2h). 248 mg (ca. 100%) was obtained as a colorless powder, mp 118–120 °C (from CCl_4/petroleum ether), by following the above procedure at −10 °C for 34 h, in which a total of 30 mL of 0.098 M (2.93 mmol) dioxirane and 233 mg (0.932 mmol) of 4′,6-dimethylflavone (**1h**) was employed. UV (CH_2Cl_2): λ_{max} (log ϵ) = 226.0 (4.327), 254.4 (4.195), 324.4 (3.824) nm. IR (CCl_4): ν = 3020 (w), 2920 (w), 1690 (s), 1620 (m), 1495 (s), 1425 (w), 1420 (w), 1390 (w), 1305 (s), 1270 (w), 1220 (s), 1185 (m), 1135 (m), 1105 (m), 1080 (w), 1015 (m), 930 (w) cm^{-1}. ^1H NMR (200 MHz, CD_2Cl_2): δ = 2.42 (s, 3 H), 2.46 (s, 3 H), 3.91 (s, 1 H), 7.16 (d, J = 8.46 Hz, 1 H), 7.35 (d, J = 7.98 Hz, 2 H), 7.49 (dd, J_1 = 8.46 Hz, J_2 = 2.29 Hz, 1 H), 7.56 (d, J = 1.82 Hz, 1 H), 7.59 (d, J = 1.60 Hz, 1 H), 7.79 (d, J = 1.60 Hz, 1 H). ^{13}C NMR (50 MHz, CD_2Cl_2): δ = 20.6 (q), 21.4 (q), 64.4 (d), 85.3 (s), 118.3 (d), 119.3 (s), 126.1 (d), 126.8 (d), 129.7 (d), 130.7 (s), 133.5 (s), 137.6 (d), 140.4 (s), 154.7 (s), 188.8 (s). MS (70 eV): m/z (rel. abund.) = 266 (12, M^+), 250 (20, $M^+ - O$), 238 (61, $M^+ - CO$), 237 (87, $M^+ - CHO$), 222 (12, $M^+ - CO_2$), 209 (14, $M^+ - C_4H_7O$), 178 (4, $M^+ - C_4H_8O_2$), 169 (11, $M^+ - C_6H_9O$), 164 (15, $M^+ - C_5H_9O_2$), 149 (17, $M^+ - C_8H_5O$), 134 (23, $M^+ - C_9H_8O$), 119 (86, $M^+ - C_9H_7O_2$), 105 (41, $M^+ - C_{10}H_9O_2$), 91 (100, $M^+ - C_{10}H_7O_3$), 77 (24, $M^+ - C_{11}H_9O_3$). Anal. Calcd for $C_{17}H_{14}O_3$ (266.3): C, 76.68; H, 5.30. Found: C, 76.23; H, 5.41.

1a,7a-Dihydro-5-methyl-1a-(4-methoxyphenyl)-7*H*-oxireno[*b*][1]benzopyran-7-one (2i). 218 mg (ca. 100%) were obtained as colorless needles, mp 113–115 °C (from CCl_4/petroleum ether), by following the above procedure at 0 °C for 23 h, in which a total of 40 mL of 0.079 M (3.18 mmol) dioxirane and 206 mg (0.770 mmol) of 4′-methoxy-6-methylflavone (**1i**) were employed. UV (CH_2Cl_2): λ_{max} (log ϵ) = 227.6 (4.542), 257.2 (4.189), 326 (3.672) nm. IR (CCl_4): ν = 3010 (w), 2980 (w), 2960 (w), 1700 (s), 1630 (m), 1530 (m), 1500 (m), 1430 (w), 1310 (m), 1280 (w), 1270 (s), 1230 (m), 1180 (s), 1140 (m), 1110 (m), 1085 (w), 1050 (m), 1030 (w), 1010 (w), 935 (w) cm^{-1}. ^1H NMR (200 MHz, CD_2Cl_2): δ = 2.37 (s, 3 H), 3.84 (s, 3 H), 3.85 (s, 1 H), 7.00 and 7.56 (AA′BB′ system, 4 H), 7.11 (d, J = 8.44 Hz, 1 H), 7.41–7.48 (m, 1 H), 7.73–7.74 (m, 1 H). ^{13}C NMR (50 MHz, CD_2Cl_2): δ = 20.6 (q), 55.7 (q), 64.4 (d), 85.4 (d), 114.5 (d), 118.3 (d), 125.6 (s), 126.8 (d), 127.7 (d), 129.8 (s), 133.5 (s), 137.6 (d), 154.8 (s), 161.3 (s), 188.9 (s). MS (70 eV): m/z (rel. abund.) = 282 (6, M^+), 266 (3, M^+ –

O), 254 (11, $M^+ - CO$), 253 (30, $M^+ - CHO$), 225 (4, $M^+ - C_2HO_2$), 211 (4, $M^+ - C_3H_3O_2$), 169 (10, $M^+ - C_5H_5O_3$), 135 (15, $M^+ - C_9H_7O_2$), 119 (11, $M^+ - C_9H_7O_3$), 105 (33, $M^+ - C_{10}H_9O_3$), 91 (40, $M^+ - C_{11}H_{11}O_3$), 71 (38, $M^+ - C_{13}H_7O_3$), 57 (100, $M^+ - C_{14}H_9O_3$), 44 (90, $M^+ - C_{16}H_{14}O_2$). Anal. Calcd for $C_{17}H_{14}O_4$ (282.3): C, 72.33; H, 5.00. Found: C, 72.75; H, 4.95.

1a,7a-Dihydro-5-methyl-1a-(4-chlorophenyl)-7*H*-oxireno-[*b*][1]benzopyran-7-one (2j). 227 mg (ca. 100%) was obtained as colorless needles, mp 123–124 °C (from $CHCl_3$/petroleum ether), by following the above procedure at ca. 20 °C for 27 h, in which a total of 35 mL of 0.098 M (3.42 mmol) dioxirane and 211 mg (0.779 mmol) of 4′-chloro-6-methylflavone (**1j**) were employed. UV (CH_2CL_2): λ_{max} (log ϵ) = 226.0 (4.372), 327.8 (3.576) nm. IR (CCl_4): ν = 3070 (w), 2970 (w), 1725 (s), 1645 (w), 1515 (m), 1440 (w), 1325 (m), 1285 (w), 1240 (m), 1190 (w), 1150 (w), 1125 (m), 1030 (m), 950, 920 (w), 620 (w) cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ = 2.34 (s, 3 H), 3.81 (s, 1 H), 7.06 (d, J = 8.46 Hz, 1 H), 7.37–7.40 (m, 1 H), 7.40 and 7.52 (AA′BB′ system, 4 H), 7.71 (d, J = 1.45 Hz, 1 H). ^{13}C NMR (63 MHz, $CDCl_3$): δ = 20.5 (q), 63.8 (d), 84.4 (s), 117.9 (d), 118.9 (s), 126.7 (d), 127.4 (d), 129.0 (d), 131.7 (s), 133.3 (s), 136.0 (s), 137.4 (d), 154.1 (s), 188.2 (s). MS (70 eV): m/z (rel. abund.) = 288 (10, $M^+ + 2$), 286 (30, M^+), 259 (23, $M^+ - C_2H_3$), 258 (34, $M^+ - CO$), 257 (57, $M^+ - CHO$), 223 (13, $M^+ - CClO$), 222 (22, $M^+ - CHClO$), 174 (17, $M^+ - C_6H_5Cl$), 141 (32, $M^+ - C_9H_5O_2$), 139 (100, $M^+ - C_9H_7O_2$), 111 (47, $M^+ - C_{10}H_7O_2$), 75 (60, $M^+ - C_{10}H_8ClO_3$). Anal. Calcd for $C_{16}H_{11}ClO_3$ (286.7): C. 67.03; H, 3.87. Found: C, 66.51; H, 3.89.

1a,7a-Dihydro-5-methyl-1a-(3-chlorophenyl)-7*H*-oxireno-[*b*][1]benzopyran-7-one (2k). 223 mg (ca. 100%) was obtained as colorless needles, mp 109–110 °C (from $CHCl_3$/petroleum ether), by following the above procedure at ca. 20 °C for 37 h, in which a total of 65 mL of 0.050 M (3.21 mmol) dioxirane and 215 mg (0.790 mmol) of 3′-chloro-6-methylflavone (**1k**) was employed. IR (CCl_4): ν = 3050 (w), 2930 (w), 1700 (s), 1630 (m), 1500 (m), 1435 (m), 1310 (s), 1265 (w), 1225 (s), 1140 (m), 1080 (m), 1025 (w), 950 (w), 875 (w), 690 (w) cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 2.34 (s, 3 H), 3.82 (s, 1 H), 7.07 (d, J = 8.46 Hz, 1 H), 7.39–7.47 (m, 4 H), 7.59–7.60 (m, 1 H), 7.69 (d, J = 1.66 Hz, 1 H). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 20.4 (q), 63.6 (d), 84.0 (s), 117.8 (s), 118.8 (d), 124.0 (d), 126.3 (d), 126.6 (d), 130.0 (d), 133.2 (s), 134.7 (s), 135.0 (s), 137.3 (d), 154.0 (s), 187.9 (s). MS (70 eV): m/z (rel. abund.) = 288 (8, $M^+ + 2$), 286 (24, M^+), 259 (25, $M^+ - C_2H_3$), 258 (50, $M^+ - CO$), 257 (54, $M^+ - CHO$), 223 (17, $M^+ - CClO$), 222 (22, $M^+ - CHClO$), 165 (8, $M^+ - C_7H_5O_2$), 139 (100, $M^+ - C_9H_7O_2$), 111 (56, $M^+ - C_{10}H_7O_3$). Anal. Calcd for $C_{16}H_{11}ClO_3$ (286.7): C, 67.03; H, 3.87. Found: C, 67.48; H, 3.75.

1a,7a-Dihydro-6-methoxy-1a-phenyl-7*H*-oxireno[*b*][1]-benzopyran-7-one (2l). 218 mg (ca. 100%) was obtained as colorless liquid, by following the above procedure at 0 °C for 26 h, in which a total of 35 mL of 0.098 M (3.42 mmol) dioxirane and 205 mg (0.843 mmol) of 5-methoxyflavone (**1l**) was employed. Epoxide **2l** was too labile for rigorous purification by distillation or column chromatography. IR (CCl_4): ν = 3100 (w), 3040 (w), 2960 (w), 1705 (s), 1625 (m), 1600 (m), 1490 (s), 1480 (m), 1450 (m), 1395 (m), 1285 (s), 1245 (m), 1225 (m), 1115 (s), 1100 (s), 1040 (w), 1020 (w), 970 (w), 920 (w), 700 (m) cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 3.86 (s, 1 H), 3.88 (s, 3 H), 6.65 (d, J = 8.39 Hz, 1 H), 6.73 (dd, J_1 = 8.39 Hz, J_2 = 0.73 Hz, 1 H), 7.39–7.47 (m, 4 H), 7.54–7.59 (m, 2 H). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 56.1 (q), 65.7 (d), 84.1 (s), 105.7 (d), 110.1 (d), 125.6 (d), 128.5 (d), 128.9 (s), 129.7 (d), 132.5 (s), 135.8 (d), 157.2 (s), 160.1 (s), 187.7 (s).

1a,7a-Dihydro-5-methoxy-1a-phenyl-7*H*-oxireno[*b*][1]-benzopyran-7-one (2m). 186 mg (ca. 100%) was obtained as colorless needles, mp 82–84 °C (from CCl_4/petroleum ether), by following the above procedure at −10 °C for 48 h, in which a total of 60 mL of 0.081 M (4.86 mmol) dioxirane and 175 mg (0.690 mmol) of 6-methoxyflavone (**1m**) was employed. IR (CCl_4): ν = 1695 (s), 1615 (w), 1500 (s), 1470 (w), 1460 (w), 1440 (m), 1350 (w), 1310 (s), 1215 (m), 1185 (m), 1130 (w), 1115 (w), 1050 (m), 1020 (m), 705 (m) cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ = 3.79 (s, 3 H), 3.84 (s, 1 H), 7.09 (d, J = 9.05 Hz, 1 H), 7.18 (dd, J_1 = 9.05 Hz, J_2 = 3.01 Hz, 1 H), 7.32 (d, J = 3.01 Hz, 1 H), 7.41–7.46 (m, 3 H), 7.57–7.61 (m, 2 H). ^{13}C NMR (63 MHz, $CDCl_3$): δ = 55.7 (q), 63.6 (d), 84.7 (s), 107.4 (d), 119.3 (s), 119.5 (d), 125.3 (d), 125.9 (d), 128.7 (d), 129.9 (d), 133.1 (s), 150.7 (s), 155.4 (s), 188.5 (s). MS (70 eV): m/z (rel. abund.) = 268 (2, M^+), 240 (2, $M^+ - CO$), 239 (2, $M^+ - CHO$), 150 (4, $M^+ - C_8H_8O$), 121 (23, $M^+ - C_8H_3O_3$), 117 (72, $M^+ - C_8H_7O_3$), 105 (15, $M^+ - C_9H_7O_3$), 82 (17, $M^+ - C_{11}H_6O_3$), 77 (10, $M^+ - C_{10}H_7O_4$), 57 (38, $M^+ - C_{13}H_7O_3$), 43 (100, $M^+ - C_{14}H_9O_3$). Anal. Calcd for $C_{16}H_{12}O_4$ (268.3): C, 71.64; H, 4.51. Found: C, 72.14; H, 4.49.

1a,7a-Dihydro-4-methoxy-1a-phenyl-7*H*-oxireno[*b*][1]-benzopyran-7-one (2n). 212 mg (ca. 100%) was obtained as colorless needles, mp 66–68 °C (from CCl_4/petroleum ether), by following the above procedure at −10 °C for 46 h, in which a total of 44 mL of 0.092 M (4.04 mmol) dioxirane and 199 mg (0.790 mmol) of 7-methoxyflavone (**1n**) were employed. UV (CH_2Cl_2): λ_{max} (log ϵ) = 239.6 (4.146), 279.6 (4.132), 300.0 (4.019) nm. IR (CCl_4): ν = 3080 (w), 3020 (w), 2960 (w), 1685 (s), 1620 (s), 1580 (m), 1500 (w), 1460 (w), 1450 (m), 1440 (m), 1355 (w), 1320 (m), 1310 (w), 1290 (m), 1275 (m), 1265 (m), 1220 (m), 1200 (m), 1165 (s), 1120 (m), 1080 (m), 1030 (m), 1015 (m) 840 (m), 700 (m) cm^{-1}. ^1H NMR (200 MHz, CD_3COCD_3); δ = 390 (s, 3 H), 3.94 (s, 1 H), 6.76 (d, J = 2.30 Hz, 1 H), 6.81 (dd, J_1 = 8.72 Hz, J_2 = 2.30 Hz, 1 H), 747–7.54 (m, 3 H), 7.66–7.72 (m, 2 H), 7.85 (d, J = 8.72 Hz, 1 H). ^{13}C NMR (50 MHz, CD_3COCD_3): δ = 56.3 (q), 63.5 (d), 86.1 (s), 102.1 (d), 112.5 (d), 113.3 (s), 126.8 (d), 129.1 (d), 129.4 (d), 130.6 (d), 134.2 (s), 159.1 (s), 167.2 (s), 186.8 (s). MS (70 eV): m/z (rel. abund.) = 268 (3, M^+), 240 (14, $M^+ - CO$), 239 (14, $M^+ - CHO$), 225 (5, $M^+ - C_2H_3O$), 211 (5, $M^+ - C_3H_5O$), 196 (3, $M^+ - C_3H_4O_2$), 151 (9, $M^+ - C_8H_5O$), 121 (30, $M^+ - C_8H_3O_3$), 119 (94, $M^+ - C_8H_5O_3$), 117 (95, $M^+ - C_8H_7O_3$), 105 (21, $M^+ - C_9H_7O_3$), 82 (23, $M^+ - C_{11}H_6O_3$), 77 (23, $M^+ - C_{10}H_7O_4$), 57 (37, $M^+ - C_{13}H_7O_3$), 43 (100, $M^+ - C_{14}H_9O_3$). Anal. Calcd for $C_{16}H_{12}O_4$ (268.3): C, 71.64; H, 4.51. Found: C, 72.16; H, 4.48.

Rearrangement of Epoxides 2b,h,i,n into Hydroxyflavones 3. 3-Hydroxy-4′-methylflavone (3b). 228 mg (ca. 100%) was obtained as yellow needles from $CHCl_3$/petroleum ether, mp 195–197 °C (lit.[24] 196–198 °C), when a solution of 228 mg (0.900 mmol) of epoxide **2b** in 1.0 mL of chloroform-*d* was left to stand at room temperature (ca. 20 °C) for 4 d.

Hydroxyflavone **3b** was also obtained quantitatively when a cooled (0 °C), stirred solution of 218 mg (0.870 mmol) of epoxide **2b** in absolute CH_2Cl_2 (5 mL) was treated with 24 mg of *p*-toluenesulfonic acid for 3 h under a N_2 atmosphere. IR (CCl_4): ν = 3420–3360 (w), 2970 (w), 2850 (w), 1635 (s), 1530 (w), 1495 (m), 1480 (m), 1435 (m), 1410 (w), 1360 (w), 1340 (m), 1315 (m), 1300 (w), 1260 (w), 1235 (w), 1215 (m), 1200 (w), 1145 (w), 1130 (w), 1120 (w), 1030 (w), 985 (w), 910 (w), 710 (w), 625 (w) cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ = 2.43 (s, 3 H), 7.06 (br s, 1 H), 7.54 (d, J = 8.24 Hz, 2 H), 7.37–7.44 (m, 1 H), 7.58 (d, J = 8.01 Hz, 1 H), 7.66–7.73 (m, 1 H), 8.16 (d, J = 8.24 Hz, 2 H), 8.25 (dd, J_1 = 8.01 Hz, J_2 = 1.52 Hz, 1 H). ^{13}C NMR (63 MHz, $CDCl_3$): δ = 21.6 (q), 118.2 (d), 120.7 (d), 124.4 (d), 125.4 (d), 127.7 (d), 128.2 (s), 129.3 (d), 135.5 (d), 138.1 (s), 140.6 (s), 145.9 (s), 155.3 (s), 173.3 (s).

4′,6′-Dimethyl-3-hydroxyflavone (3h). 248 mg (ca. 100%) was obtained as yellow powder from $CHCl_3$/petroleum ether, mp 193–194 °C (lit.[25] mp not given), when a solution of 248 mg (0.932 mmol) of epoxide **2h** in 1.0 mL of chloroform-*d* was left to stand at room temperature (ca. 20 °C) for 12 h. IR (CCl_4): ν = 3430–3360 (w), 3070 (w), 2960 (w), 1635 (s), 1660 (m), 1530 (m), 1510 (m), 1430 (w), 1410 (m), 1360 (w), 1340 (m), 1300 (m), 1290 (w), 1240 (w), 1230 (w), 1200 (w), 1185 (m), 1150 (w), 1120 (w), 1025 (w) cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ = 2.43 (s, 3 H), 2.46 (s, 3 H), 7.04 (br, s, 1 H), 7.33 (d, J = 8.32 Hz, 2 H), 7.44–7.52 (m, 2 H), 8.01 (s, 1 H), 8.14 (d, J = 8.32 Hz, 2 H). ^{13}C NMR (63 MHz, $CDCl_3$): δ = 20.9 (q), 21.5 (q), 118.0 (d), 120.4 (s), 124.4 (d), 127.7 (d), 128.4 (s), 129.3 (d), 134.4 (s), 134.9 (d), 138.1 (s), 140.5 (s), 145.1 (s), 153.7 (s), 173.5 (s).

3-Hydroxy-4′-methoxy-6-methylflavone (3i). 248 mg (ca. 100%) was obtained as yellow powder from EtOH, mp 192–193 °C (lit.[26] 192–193 °C), when a solution of 218 mg (0.77 mmol) of epoxide **2i** in 1.0 mL chloroform-*d* was left to stand at room

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temperature (ca. 20 °C) for 12 h. IR (CCl_4): ν = 3380–3320 (w), 2940 (w), 1620 (s), 1610 (s), 1520 (m), 1495 (w), 1465 (w), 1400 (w), 1335 (w), 1295 (m), 1270 (m), 1225 (w), 1195 (m), 1180 (m), 1140 (w), 1115 (m), 1050 (w), 920 (w) cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ = 2.47 (s, 3 H), 3.89 (s, 3 H), 7.01–7.07 (m, 1 H), 7.04 and 8.23 (AA'BB' system, 4 H), 7.45–7.52 (m, 2 H), 8.01 (br s, 1 H). ^{13}C NMR (63 MHz, $CDCl_3$): δ = 20.9 (q), 55.4 (q), 114.0 (d), 117.9 (d), 120.4 (s), 123.6 (s), 124.5 (d), 129.5 (d), 134.4 (s), 134.8 (d), 137.6 (s), 145.2 (s), 153.6 (s), 161.0 (s), 173.0 (s).

3-Hydroxy-5-methoxyflavone (3n). 218 mg (ca. 100%) was obtained as yellow needles from EtOH, mp 174–176 °C (lit.[27] 172 °C), when a solution of 218 mg (0.843 mmol) of epoxide **2n** in 1.0 mL of chloroform-*d* was left to stand at room temperature (ca. 20 °C) for 24 h. IR (CCl_4): ν = 3350–3290 (w), 2960 (w), 2850 (w), 1630 (s), 1595 (m), 1445 (w), 1420 (w), 1355 (m), 1335 (m), 1275 (m), 1215 (m), 1195 (w), 1175 (w), 1125 (w), 1110 (m), 1105 (w), 1080 (w), 1035 (w), 1010 (w), 945 (w), 710 (m), 695 (m), 665 (w) cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ = 3.93 (s, 3 H), 6.71 (d, J = 9.27 Hz, 1 H), 7.04 (d, J = 8.54 Hz, 1 H), 7.39–7.45 (m, 5 H), 8.16 (m, 2 H). ^{13}C NMR (63 MHz, $CDCl_3$): δ = 56.3 (q), 104.9 (d), 110.2 (d), 127.3 (d), 128.5 (d), 128.8 (s), 129.8 (s), 130.8 (s), 133.9 (d), 138.5 (s), 142.3 (s), 157.1 (s), 159.4 (s), 172.7 (s).

3-Hydroxy-2-methoxyflavanones 4b,f from Methanolysis of Epoxides 2. 3-Hydroxy-2-methoxy-4′-methylflavanone (4b). A solution of epoxide **2b** (227 mg, 0.900 mmol) in methanol (30 mL) was stirred at 0 °C for 12 h under a N_2 atmosphere. The solvent was evaporated (ca. 20 °C (15 Torr)), and flavanone **4b** (255 mg, ca. 100%) was isolated as a colorless powder, mp 136–156 °C, (from $CHCl_3$/petroleum ether). IR (CCl_4): ν = 3640–3600 (w), 3520–3480 (w), 3060 (w), 3020 (w), 2980 (w), 2960 (w), 2850 (w), 1720 (s), 1620 (s), 1595 (m), 1525 (m), 1475 (s), 1315 (m), 1240 (m), 1190 (m), 1145 (m), 1100 (m), 1030 (m), 980 (m), 700 (w), 670 (w) cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ = 2.36 (s, 3 H), 3.11 (s, 3 H), 3.13 (s, 1 H), 4.28 (d, J = 4.48 Hz, 1 H), 7.04–7.11 (m, 1 H), 7.14–7.24 (m, 3 H), 7.51 (d, J = 8.37 Hz, 2 H), 7.53–7.60 (m, 1 H), 7.84 (dd, J_1 = 7.79 Hz, J_2 = 0.68 Hz, 1 H). ^{13}C NMR (63 MHz, $CDCl_3$): δ = 21.2 (q), 50.4 (q), 74.9 (d), 106.4 (d), 117.9 (d), 119.2 (s), 122.2 (d), 127.2 (d), 127.3 (d), 129.3 (d), 132.1 (s), 136.5 (d), 139.3 (s), 157.4 (s), 191.7 (s). MS (70 eV): m/z (rel. abund.) = 284 (51, M^+), 252 (100, $M^+ - CH_4O$), 237 (18, $M^+ - C_2H_7O$), 224 (17, $M^+ - C_3H_8O$), 223 (27, $M^+ - C_2H_5O_2$), 164 (29, $M^+ - C_9H_{12}$), 149 (17, $M^+ - C_9H_{11}O$), 135 (11, $M^+ - C_9H_9O_2$), 121 (93, $M^+ - C_{10}H_{11}O_2$), 119 (49, $M^+ - C_{9H9}O_3$), 105 (12, $M^+ - C_{10}H_{11}O_3$), 93 (22, $M^+ - C_{11}H_{11}O_3$), 91 (33, $M^+ - C_{11}H_{13}O_3$), 77 (15, $M^+ - C_{11}H_{11}O_4$). Anal. Calcd for $C_{17}H_{16}O_4$ (284.3): C, 71.82; H, 5.67. Found: C, 72.34; H, 5.93.

3′-Chloro-3-hydroxy-2-methoxyflavanone (4f). According to the above procedure, a solution of epoxide **2f** (212 mg, 0.78 mmol) in methanol (10 mL) was stirred at ca. 20 °C for 24 h under a N_2 atmosphere. The residue, after evaporation of the solvent (ca. 20 °C (15 Torr), gave after repeated recrystallizations from CCl_4/petroleum ether flavanone **4f** (158 mg, ca. 100% at 67% conversion) as colorless needles, mp 138–143 °C. IR (CCl_4): ν = 3640–3620 (w), 3520–3480 (w), 2940 (w), 2860 (w), 1700 (m), 1605 (m), 1580 (w), 1470 (w), 1460 (m), 1420 (w), 1370 (w), 1305 (m), 1140 (m), 1090 (s), 1060 (m), 1025 (m), 1000 (m), 990 (m), 950 (w), 720 (m), 700 (m) cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ = 3.14 (s, 4 H), 4.28 (d, J = 3.92 Hz, 1 H), 7.10–7.20 (m, 2 H), 7.37–7.43 (m, 2 H), 7.49–7.53 (m, 1 H), 7.58–7.65 (m, 1 H), 7.68–7.69 (m, 1 H), 7.88 (dd, J_1 = 7.77 Hz, J_2 = 1.66 Hz, 1 H). ^{13}C NMR (63 MHz, $CDCl_3$): δ = 50.6 (q), 74.6 (d), 105.6 (s), 117.9 (d), 119.0 (s), 122.6 (d), 125.4 (d), 127.4 (d), 127.8 (d), 129.6 (d), 129.9 (d), 134.7 (s), 136.8 (d), 137.4 (s), 157.0 (s), 191.2 (s). MS (70 eV): m/z (rel. abund.) = 306 (6, $M^+ + 2$), 304 (18, M^+), 274 (6, $M^+ - CH_2O$), 273 (21, $M^+ - CH_3O$), 272 (55, $M^+ - CH_4O$), 243 (15, $M^+ - C_2H_2O_2$), 209 (12, $M^+ - C_6H_7O$), 184 (11, $M^+ - C_4H_5ClO_2$), 181 (10, $M^+ - C_7H_7O_2$), 152 (15, $M^+ - C_8H_8O_3$), 141 (11, $M^+ - C_9H_4ClO$), 139 (32, $M^+ - C_9H_6ClO$), 121 (100, $M^+ - C_9H_8ClO_2$), 111 (25, $M^+ - C_{10}H_6ClO_2$), 105 (15, $M^+ - C_9H_8ClO_3$), 93 (12, $M^+ - C_{10}H_8ClO_3$), 77 (41, $M^+ - C_{10}H_8ClO_4$), 76 (20, $M^+ - C_{10}H_9ClO_4$). Anal. Calcd for $C_{16}H_{13}ClO_4$ (304.7): C, 63.07; H, 4.30. Found: C, 63.32; H, 4.38.

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Supplementary Material Available: ^1H and ^{13}C NMR spectra of epoxide **2l** (2 pages). Ordering information is given on any current masthead page.

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On the Iconic Nature of Conformational Pictures and Their Recognition

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An algorithm for recognition of hand-drawn conformational pictures is presented in the form of a program "ZED". The problem is defined and discussed in terms of "unprojection", creation of a three-dimensional object from a conformational picture. The behavior of ZED is illustrated with numerous stereoscopic views of the results of unprojection. An unexpected limitation to unprojection is encountered: the fact that conformational pictures are *icons*, not actual projections.

Central to organic chemistry is the problem of *representation* of organic molecules, the relationship between the molecular objects, and our pictures and models thereof.[1,2] We deal here with the question of machine

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