A Comparative Study of the Epoxidation of 2-Substituted Isoflavones by Dimethyldioxirane, Sodium Hypochlorite, and Alkaline Hydrogen Peroxide (Weitz-Scheffer Reaction)

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Dedicated to the memory of Professor Raymond N. Castle

The comparative epoxidation of 2-substituted isoflavones **9-16** has been conducted by the utilization of three different protocols, *viz.* epoxidation with isolated dimethyldioxirane (Method A), with sodium hypochlorite (Method B), and with alkaline hydrogen peroxide (Method C), to afford epoxides **17-24**. Best results have been obtained with Method C (Weitz-Scheffer epoxidation). The structures of epoxides have been assigned on the basis of nmr spectral and mass spectral data.

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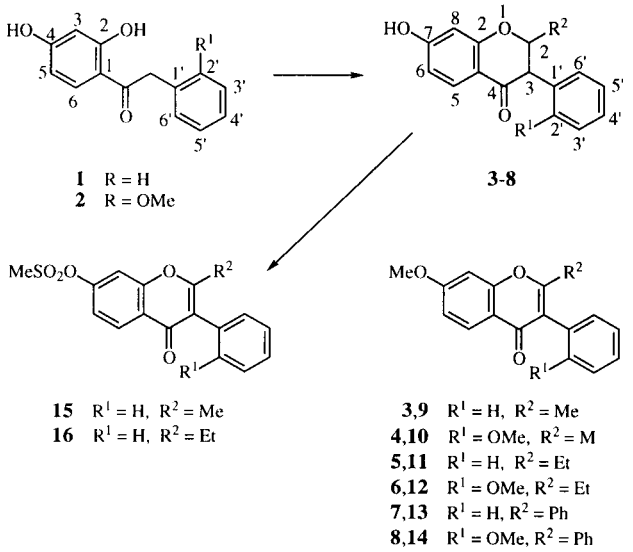
Isoflavones are well-known natural products isolated from various plant sources [1,2]. Despite this fact, prior to our own studies, their epoxidation has received little attention. The first representatives of the isoflavone epoxides were prepared by the alkaline hydrogen peroxide epoxidation of the appropriate isoflavones [3-5] or by an intramolecular Darzens reaction of α-bromo-*o*-acyloxydeoxybenzoins [6,7]. However, the very limited number of examples does not allow one to reach any conclusion about scope and generality.

Recently we have demonstrated that dimethyldioxirane (DMD) is a convenient and highly effective reagent for the epoxidation of variously substituted flavones [8], isoflavones [9] and isoflavone glycosides [10], which afford the particular epoxides in high yields, without the need of purification. Moreover, we have succeeded in the enantioselective epoxidation of isoflavones by using optically active Jaconsen's Mn(III)salen catalysts in combination with dimethyldioxirane or sodium hypochlorite as oxygen-atom sources [11,12]. These results provided the first examples for the preparation of optically active isoflavone epoxides.

Epoxides of few 2-substituted isoflavones have been synthesized by Donnelly and Maloney [7] by intramolecular Darzens reaction of α-bromo-*o*-acyloxydeoxybenzoins, but the overall yields were generally less than 20%. For this reason, this protocol cannot be considered as an adequate procedure for the synthesis of such chromone epoxides. Furthermore, the only example for the epoxidation of a 2-substituted isoflavone is the alkaline hydrogen peroxide epoxidation of the 2-methylisoflavone [4]. In view of these facts, it appeared expedient to perform a detailed investigation of the epoxidation of 2-substituted isoflavones. One of the aims of our present study was to assess the steric influence of the substituent at position 2 in the isoflavone molecule. For this purpose, 2-methyl-, 2-ethyl- and 2-phenylisoflavones have been used as substrates. The efficacy and utility of three different procedures have been compared: Epoxidation with isolated dimethyldioxirane (Method A) [13], sodium hypochlorite (Method B) [14], and alkaline hydrogen peroxide (Method C) [15].

Some of the substrates **9-16** are known compounds (**9-11** and **13**), which were synthesized as described in the literature [16-19]. Substances **12** and **14-16** are new compounds and have been prepared by starting from 2,4-dihydroxydeoxybenzoins **1** and **2** [20,21], as outlined in the Experimental. 7-Methoxyisoflavones **9-14** proved to be convenient substrates for this purpose since their synthesis is simple. In the case of the enantioselective epoxidation of isoflavones [11,12], the presence of a methoxy group in the vicinity of the double bond proved to be beneficial as far as the enantiofacial differentiation is concerned. Since we have planned to perform the enantioselective epoxidation of 2-substituted isoflavones as well, the influence of a methoxy group at position 2' of the isoflavone molecule has also been investigated.

Scheme 1



1 R = H
2 R = OMe

3-8

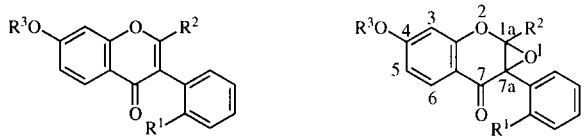
15 R^1 = H, R^2 = Me
16 R^1 = H, R^2 = Et

3,9 R^1 = H, R^2 = Me
4,10 R^1 = OMe, R^2 = M
5,11 R^1 = H, R^2 = Et
6,12 R^1 = OMe, R^2 = Et
7,13 R^1 = H, R^2 = Ph
8,14 R^1 = OMe, R^2 = Ph

As mentioned above, the dimethyldioxirane proved to be a convenient and powerful oxidant for the epoxidation of isoflavones [9] and their glycosides [10]. For this reason, 2-substituted isoflavones **9-16** were allowed to react with isolated dimethyldioxirane (0.05-0.1*M* acetone solution) according to Method A. The progress of the reaction was monitored by thin layer chromatography (tlc), and fresh batches of dimethyldioxirane solution were added in 24 hour intervals until the consumption of the starting material halted (15 days). No complete conversion of the substrate could be achieved even during such prolonged reaction times and by using up to 23 equivalents of dimethyldioxirane. The conversion varied between 40-50%. As a result, the yields of the isolated epoxides were not higher than 14-38%. The incomplete conversion of the starting material is the consequence of the electron-poor double bond. Neither the space demand of the substituent at position 2 of the isoflavone molecule nor the presence of a 2'-methoxy group influenced either the conversion of the starting material or the yield of the epoxidation.

Since the electrophilic dimethyldioxirane proved to be ineffective for the epoxidation of 2-substituted isoflavones, the utility of two well-known nucleophilic oxidizing agents, *viz.* sodium hypochlorite (Method B) and alkaline hydrogen peroxide (Method C) was explored. Our experimental results (*cf.* Experimental) demonstrate that the sodium hypochlorite is a convenient oxidant for the epoxidation of the 2-methyl- and 2-ethylisoflavones **9-12** providing 66-75% yields on a complete conversion of the starting isoflavones. However, mesyl esters **15** and **16** suffered considerable decomposition under these alkaline reaction conditins. A careful chromatographic separation of the multicomponent reaction mixtures provided their epoxides **23** and **24** as the only isolable products in low (10 and 19%) yields. Moreover, in the case of the 2-phenylisoflavones **13** and **14**, only 50% conversion of the starting material was obtained even during a prolonged (24 hour) reaction time resulting again in low (23 and 38%) yields of the isolated products. This low reactivity of these isoflavones may be due to the steric overcrowded double bond.

Scheme 2



9-16 **17-24**

9,17 R^1 = H, R^2 = R^3 = Me
10,18 R^1 = OMe, R^2 = R^3 = Me
11,19 R^1 = H, R^2 = Et, R^3 = Me
12,20 R^1 = OMe, R^2 = Et, R^3 = Me
13,21 R^1 = H, R^2 = Ph, R^3 = Me
14,22 R^1 = OMe, R^2 = Ph, R^3 = Me
15,23 R^1 = H, R^2 = Me, R^3 = $MeSO_2$
16,24 R^1 = H, R^2 = Et, R^3 = $MeSO_2$

To overcome the shortcomings encountered with dimethyldioxirane (Method A) and sodium hypochlorite (Method B), the isoflavones **9-14** were allowed to react with alkaline hydrogen peroxide (Method C) and their corresponding epoxides **17-22** have been obtained in good (67-88%) yields on a complete conversion of the starting materials. Since the ester group is sensitive to such a strongly alkaline medium, the epoxidation of derivatives **15** and **16** have not been conducted by this method. Our experimental results establish that the alkaline hydrogen peroxide (Weitz-Scheffer epoxidation) is an adequate nucleophilic oxidant for the epoxidation of the electron-poor 2-substituted isoflavones, irrespective of the steric bulk of the substituent at position 2 of the isoflavone molecule.

The structures of the epoxides **17-24** have been elucidated by ^1H and ^{13}C nmr spectroscopic measurements and by their mass spectra. Since no hydrogen atom is connected to the double bond of the chromone skeleton, in the ^1H nmr spectra no considerable changes take place on the epoxidation. Only an upfield shift of *ca.* $\Delta\delta$ 0.6 ppm for the singlet signal of the 2-methyl group (epoxides **17**, **18** and **23**) and a splitting of the AB quartet signal of the methylene group of the 2-ethylisoflavone epoxides **19**, **20** and **24** were observed. However, all proposed structures of the epoxides **17-24** are in full accord with their ^1H nmr spectra. In contrast, the ^{13}C nmr spectra change characteristically on epoxidation of 2-substituted isoflavones **9-16**. The olefinic signals of the C-2 and C-3 atoms of the isoflavone skeleton have been replaced by the characteris-

tic epoxide C-1a (89-91 ppm) and C-7a (66-70 ppm) signals in the ^{13}C nmr spectra, which unequivocally establishes the presence of the epoxide functionality. A downfield shift of about 10 ppm was detected in the signal for the C-7 atom of the carbonyl group (*ca.* 186-187 ppm) of epoxides **17-24**. Similar ^{13}C nmr shifts were measured for the C-1a, C-7a, and C-7 atoms in the epoxides of the isoflavones unsubstituted at position 2 [9-12].

The mass spectra of the epoxides **17-24** display relatively strong molecular ions (relative intensity 2-19%). As major fragmentation step of the molecular ion, a characteristic ion is formed from the loss of a R^2(C-2)O fragment (after hydrogen-transfer), if R^2 is either a methyl or an ethyl group. The next step is the loss of the R^3 group from the OR^3 substituent. Formation of an R^3CO ion occurs also in the fragmentation of these isoflavone epoxides. The detection of a molecular ion and the characteristic fragmentations corroborate the presence of an epoxide functionality in the molecule.

In summary, as may be expected for the electron-poor and sterically crowded 2-substituted isoflavones, a nucleophilic oxidant is the reagent of choice for the epoxidation of these substrates. For this purpose, best results (high conversions, good yields) have been achieved with alkaline hydrogen peroxide (Method C, Weitz-Scheffer epoxidation [15]). Also the nucleophilic sodium hypochlorite (Methods B) performs adequately, but not as well. The electrophilic dimethyldioxirane is quite ineffective (low coversions, poor yields) even at long reaction times and large excess of reagent. Besides the electron deficiency of the double bond to be epoxidized in the isoflavone substrate, steric effects of the rather crowded double bond in the 2-phenyl derivatives (2,3-diphenylchromones) appear to be responsible for the low reactivity towards the dioxirane. Since all but **17** are new compounds, previously unknown 2-substituted isoflavone epoxides became easily accessible by using these protocols.

EXPERIMENTAL

Melting points were determined on a Kofler hot-stage apparatus and are uncorrected. ^1H and ^{13}C nmr spectra were recorded on a Gemini 200 spectrometer with tetramethylsilane as the internal standard. Mass spectra were taken on a VG Trio-2 (EI, 70 eV) apparatus. Elemental analyses were measured in house on a Carlo Erba 1106 EA instrument. The tlc was performed on Kieselgel 60 F_{254} (Merck) layer with hexane-acetone (7:3 v/v) or toluene-ethyl acetate (4:1 v/v) as eluents. The starting materials **1-5**, **7**, **9**, **10**, **11** and **13** were synthesized according to known procedures [16-21]. Dimethyldioxirane (DMD, as 0.05-0.1*M* acetone solution) was prepared as described [22] and its peroxide content was determined iodometrically. Curox (potassium monoperoxosulfate), the triple salt $2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$, was used as received, a generous gift from the Peroxid-Chemie GmbH (München, Germany).

2-Ethyl-7-hydroxy-3-(2-methoxyphenyl)chromen-4-one (**6**).

A mixture of 2,4-dihydroxy-2'-methoxydeoxybenzoin [21] (**2**, 10.0 g, 41 mmoles), propionic anhydride (100.0 ml) and triethyl amine (50.0 ml) was refluxed for 5 hours, then poured onto crushed ice and acidified with hydrochloric acid. The precipitate was removed by filtration, washed free of acid, and refluxed in a mixture of methanol (100.0 ml) and 2*M* sodium hydroxide solution (50.0 ml) for 10 minutes. The solution was cooled to room temperature (*ca.* 20°) and acidified with hydrochloric acid. The precipitate was collected, washed free of acid and recrystallized from methanol to yield 3.40 g (29%), mp 193-194°, white needles; ^1H nmr: δ 1.21 (3H, t, J = 7.57 Hz, CH_3), 2.50 (2H, m, CH_2CH_3), 3.70 (3H, s, OMe), 6.74-7.98 (7 arom H, m), 9.85 (1H, s, OH); ^{13}C nmr: δ 11.3, 26.1, 55.3, 102.5, 111.1, 115.6, 115.8, 118.9, 120.8, 121.9, 127.4, 129.8, 131.9, 157.7, 158.4, 163.3, 168.6, 178.2.

Anal. Calcd. for $C_{18}H_{16}O_4$: C, 72.96; H, 5.44. Found: C, 72.89; H, 5.46.

7-Hydroxy-3-(2-methoxyphenyl)-2-phenylchromen-4-one (**8**).

A mixture of 2,4-dihydroxy-2'-methoxydeoxybenzoin [21] (**2**, 8.00 g, 33 mmoles), benzoic anhydride (30.0 g) and triethyl amine (75.0 ml) was refluxed for 8 hours, then worked up as described for compound **6** to afford 6.80 g (63%), mp 258-259°, white plates; ^1H nmr: δ 3.58 (3H, s, OMe), 6.82-7.94 (12 arom H, m), 10.84 (1H, s, OH); ^{13}C nmr: δ 55.2, 102.3, 111.4, 115.3, 115.6, 119.3, 120.4, 122.7, 127.3, 128.2, 128.5, 129.5, 130.1, 132.2, 133.5, 157.6, 157.7, 160.8, 163.0, 175.5.

Anal. Calcd. for $C_{22}H_{16}O_4$: C, 76.73; H, 4.68. Found: C, 76.68; H, 4.65.

2-Ethyl-7-methoxy-3-(2-methoxyphenyl)chromen-4-one (**12**).

A mixture of 2-ethyl-7-hydroxy-3-(2-methoxyphenyl)-chromen-4-one (**6**, 2.96 g, 10.0 mmoles), methyl iodide (3.0 ml, 48.4 mmoles), potassium carbonate (10.0 g) and anhydrous acetone (100.0 ml) was refluxed for 6 hours, then the inorganic precipitate was removed by filtration. The solvent was evaporated *in vacuo* and the residue was recrystallized from methanol to obtain 2.50 g (81%), mp 120-121°, white needles; ^1H nmr: δ 1.21 (3H, t, J = 7.57 Hz, CH_3), 2.48 (2H, m, CH_2CH_3), 3.74 (3H, s, OMe), 3.90 (3H, s, OMe), 6.85-8.13 (7 arom H, m); ^{13}C nmr δ 11.2, 25.9, 55.4, 55.6, 99.9, 111.2, 113.9, 117.5, 119.3, 120.7, 122.4, 127.8, 129.5, 132.1, 157.6, 157.9, 163.9, 167.3, 176.6.

Anal. Calcd. for $C_{19}H_{18}O_4$: C, 73.53; H, 5.84. Found: C, 73.57; H, 5.82.

7-Methoxy-3-(2-methoxyphenyl)-2-phenylchromen-4-one (**14**).

A mixture of 7-hydroxy-3-(2-methoxyphenyl)-2-phenylchromen-4-one (**8**, 1.72 g, 5.0 mmoles), methyl iodide (1.5 ml, 24.2 mmoles), potassium carbonate (5.00 g) and anhydrous acetone (150.0 ml) was allowed to react as described for compound **12** to afford 1.30 g (78%), mp 187-188°, white needles; ^1H nmr: δ 3.58 (3H, s, OMe), 3.89 (3H, s, OMe), 6.83-8.19 (12 arom H); ^{13}C nmr δ 55.3, 55.6, 95.9, 100.1, 111.2, 114.3, 117.4, 119.8, 120.7, 122.6, 127.8, 127.9, 128.7, 129.5, 129.8, 132.3, 133.9, 157.7, 158.0, 161.5, 164.2, 176.7.

Anal. Calcd. for $C_{23}H_{18}O_4$: C, 77.08; H, 5.06. Found: C, 77.12; H, 5.04.

7-Mesyloxy-2-methyl-3-phenylchromen-4-one (**15**).

Mesyl chloride (10.0 ml) was added in small portions to a cooled and stirred mixture of 7-hydroxy-2-methylisoflavone [13] (**3**, 5.00 g, 20.0 mmoles) and anhydrous pyridine (60.0 ml). The mixture was left to stand in the refrigerator (*ca.* 5°) for 72 hours, then poured onto crushed ice and acidified with hydrochloric acid. The precipitate was collected, washed with water, and recrystallized from methanol to obtain 4.20 g (64%), mp 156-157°, white needles; ^{1}H nmr: δ 2.31 (3H, s, Me), 3.22 (3H, s, $MeSO_2$), 7.25-8.27 (8 arom H, m); ^{13}C nmr: δ 19.2, 37.8, 111.3, 118.9, 122.4, 124.0, 128.1, 128.5, 130.4, 132.6, 152.3, 156.4, 164.1, 175.9.

Anal. Calcd. for $C_{17}H_{14}O_5S$: C, 61.82; H, 4.27. Found: C, 61.88; H, 4.25.

2-Ethyl-7-mesyloxy-3-phenylchromen-4-one (**16**).

2-Ethyl-7-hydroxyisoflavone [15] (**5**, 2.66 g, 10.0 mmoles) was dissolved in anhydrous pyridine (30.0 ml) and allowed to react with mesyl chloride (5.0 ml) as described for compound **15** to afford 3.00 g (87%), mp 117-118°, white plates; ^{1}H nmr: δ 1.27 (3H, t, J = 7.57, CH_3), 2.59 (2H, dd, J = 15.02, 7.53 Hz, CH_2CH_3), 3.21 (3H, s. $MeSO_2$), 7.22-8.27 (8 arom H, m); ^{13}C nmr: δ 11.6, 25.9, 37.8, 111.3, 118.8, 122.4, 123.4, 128.0, 128.4, 128.5, 130.3, 132.6, 152.4, 156.5, 168.1, 176.2.

Anal. Calcd. for $C_{18}H_{16}O_5S$: C, 62.78; H, 4.68. Found: C, 62.71; H, 4.64.

General Procedures for the Epoxidation of 2-Substituted Isoflavones **9-16**.

Method A.

Dimethyldioxirane (*ca.* 0.05-0.1*M* acetone solution) was added to a stirred solution of the appropriate isoflavone **9-16** (0.50 g, 1.39-1.87 mmoles) in anhydrous methylene chloride (10.0 ml) and the agitation was continued at room temperature (*ca.* 20°). The progress of the reaction was monitored by tlc and new batches of dimethyldioxirane were added in 24 hour intervals until the conversion of the starting material halted (*ca.* 15 days). The solvent was evaporated *in vacuo* and the epoxides **17-24** were purified by silica gel chromatography with toluene:ethyl acetate (4:1 v/v) as eluent.

Method B.

Sodium hypochlorite solution (8.0-12.0 ml, 5.0-6.0 mmoles) was added to a stirred solution of the appropriate isoflavone **9-16** (0.5 g, 1.39-1.87 mmoles) in pyridine (25.0 ml) and the stirring was continued at room temperature (*ca.* 20°) for 2 hours. The solution was diluted with water, the precipitated material was collected, washed with water, and recrystallized from methanol or purified by silica gel chromatography with toluene:ethyl acetate (4:1 v/v) as eluent to afford the epoxides **17-24**.

Method C (Weitz-Scheffer Epoxidation).

Hydrogen peroxide (30%, 1.0 ml, 8.82 mmoles) was added to a cooled and stirred mixture of the particular isoflavone **9-14** (0.50 g, 1.39-1.87 mmoles) and 4*M* sodium hydroxide solution (1.0 ml, 4 mmoles) in methanol (40 ml). The agitation was continued at ambient temperature (*ca.* 20°) for 16 hours, then the solution was diluted with water, the precipitated material was collected, washed with water, and recrystallized from methanol to yield the epoxides **17-22**.

1a,7a-Dihydro-4-methoxy-1a-methyl-7a-phenyl-7*H*-oxireno[*b*]-[1]benzopyran-7-one (**17**).

This epoxide was obtained as white needles in 38% (Method A), 70% (Method B) and 67% (Method C) yields, mp 134-135° (Lit. [7] mp 133°); ^{1}H nmr: δ 1.63 (3H, s, Me), 3.88 (3H, s, OMe), 6.52-7.96 (8 arom H, m); ^{13}C nmr: δ 55.6, 67.9, 88.6, 100.9, 111.5, 113.3, 127.6, 128.3, 128.8, 129.5, 130.6, 157.6, 166.3, 187.7.

Anal. Calcd. for $C_{17}H_{14}O_4$: C, 72.33; H, 4.99. Found: C, 72.29; H, 4.97.

1a,7a-Dihydro-4-methoxy-7a-(2-methoxyphenyl)-1a-methyl-7*H*-oxireno[*b*][1]benzopyran-7-one (**18**).

This epoxide was prepared as white needles in 14% (Method A), 75% (Method B) and 85% (Method C) yields, mp 114-115°; ^{1}H nmr: δ 1.60 (3H, s, Me), 3.74 (3H, s, OMe), 3.87 (3H, s, OMe), 6.54-7.92 (7 arom H, m); ^{13}C nmr: δ 55.5, 66.2, 88.4, 100.9, 110.4, 111.2, 112.6, 120.8, 129.4, 129.6, 130.1, 157.4, 157.8, 166.1, 186.7.

Anal. Calcd. for $C_{18}H_{16}O_5$: C, 69.22; H, 5.16. Found: C, 69.25; H, 5.14.

1a,7a-Dihydro-1a-ethyl-4-methoxy-7a-phenyl-7*H*-oxireno[*b*]-[1]benzopyran-7-one (**19**).

This epoxide was prepared as white needles in 38% (Method A), 66% (Method B) and 76% (Method C) yields, mp 115-116°; ^{1}H nmr: δ 1.11 (3H, t, J = 7.49 Hz, CH_3), 1.68 (1H, m, CH_2CH_3), 1.93 (1H, m, CH_2CH_3), 3.76 (3H, s, OMe), 6.56-7.91 (8 arom H, m); ^{13}C nmr: δ 7.9, 24.6, 55.6, 68.4, 91.3, 100.9, 111.5, 113.4, 127.6, 128.2, 128.7, 129.5, 130.6, 157.9, 166.3, 187.8.

Anal. Calcd. for $C_{18}H_{16}O_4$: C, 72.96; H, 5.44. Found: 72.91; H, 5.41.

1a,7a-Dihydro-1a-ethyl-4-methoxy-7a-(2-methoxyphenyl)-7*H*-oxireno[*b*][1]benzopyran-7-one (**20**).

This epoxide was obtained as white needles in 17% (Method A), 71% (Method B) and 88% (Method C) yields, mp 129-130°; ^{1}H nmr: δ 1.10 (3H, t, J = 7.53 Hz, CH_3), 1.67 (1H, m, CH_2CH_3), 1.89 (1H, m, CH_2CH_3), 3.74 (3H, s, OMe), 3.87 (3H, s, OMe), 6.54-7.93 (7 arom H, m); ^{13}C nmr: δ 7.9, 24.8, 55.3, 66.6, 91.1, 100.9, 110.4, 111.3, 112.6, 120.8, 128.5, 129.5, 130.1, 157.4. 158.1, 166.1, 186.6.

Anal. Calcd. for $C_{19}H_{18}O_5$: C, 69.93; H, 5.56. Found C, 69.97; H, 5.54.

1a,7a-Dihydro-1a,7a-diphenyl-4-methoxy-7*H*-oxireno[*b*][1]-benzopyran-7-one (**21**).

This epoxide was prepared as white plates in 16% (Method A), 23% (Method B) and 72% (Method C) yields, mp 172-173°; ^{1}H nmr: δ 3.88 (3H, s, OMe), 6.61-7.98 (13 arom H, m); ^{13}C nmr: δ 55.7, 70.52, 90.0, 101.2, 112.0, 113.4, 127.4, 127.6, 127.9, 128.5, 129.6, 129.7, 129.8, 131.7, 158.2, 166.4, 187.1.

Anal. Calcd. for $C_{22}H_{16}O_4$: C, 76.73; H, 4.68. Found: C, 76.78; H, 4.66.

1a,7a-Dihydro-4-methoxy-7a-(2-methoxyphenyl)-1a-phenyl-7*H*-oxireno[*b*][1]benzopyran-7-one (**22**).

This epoxide was obtained as white plates in 19% (Method A), 38% (Method B) and 81% (Method C) yields, mp 107-108°; ^{1}H nmr: δ 3.54 (3H, s, OMe), 3.90 (3H, s, OMe), 6.60-8.04 (12 arom H, m); ^{13}C nmr: δ 55.6, 89.9, 101.2, 110.2, 111.8, 112.3, 120.4,

126.2, 127.2, 127.7, 127.8, 128.5, 128.8, 129.4, 129.7, 129.9, 130.1, 132.0, 156.9, 158.4, 166.3, 186.3.

Anal. Calcd. for $C_{23}H_{18}O_5$: C, 73.78; H, 4.84. Found: C, 73.74; H, 4.86.

1a,7a-Dihydro-1a-methyl-4-mesyloxy-7a-phenyl-7*H*-oxireno-[*b*][1]benzopyran-7-one (**23**).

This epoxide was obtained as white needles in 23% (Method A) and 10.0% (Method B) yields, mp 113-114°; ^{1}H nmr: δ 1.66 (3H, s, Me), 3.22 (3H, s, $MeSO_2$), 7.03-8.04 (8 arom H, m); ^{13}C nmr: δ 17.4, 37.9, 68.4, 88.9, 111.4, 116.9, 118,8, 127.6, 128.5, 128.7, 129.1, 129.8, 129.9, 154.5, 156.5, 187.9.

Anal. Calcd. for $C_{17}H_{14}O_6S$: C, 58.96; H, 4.07. Found: C, 58.93; H, 4.09.

1a,7a-Dihydro-1a-ethyl-4-mesyloxy-7a-phenyl-7*H*-oxireno[b]-[1]benzopyran-7-one (**24**).

This epoxide was obtained as white needles in 27% (Method A) and 19% (Method B) yields, mp 117-118°; ^{1}H nmr: δ 1.12 (3H, t, J = 7.41 Hz, CH_3), 1.74 (1H, m, CH_2CH_3), 1.96 (1H, m, CH_2CH_3), 3.43 (3H, s, $MeSO_2$), 7.07-8.05 (8 arom H, m); ^{13}C nmr: δ 7.9, 24.5, 37.9, 68.9, 91.6, 111.5, 116,9, 118.9, 127.6, 128.4, 128.6, 129.0, 129.7, 129.9., 154.5, 156.8, 187.9.

Anal. Calcd. for $C_{18}H_{16}O_6S$: C, 59.99; H, 4.47. Found: C 59.94; H, 4.49.

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