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Studies on Quinones. 28[1]. Novel Rearrangements of Diels-Alder Adducts of Naphtho- and Anthradiquinones

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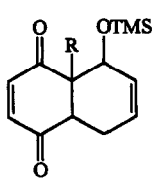
Abstract· The Diels-Alder adducts **7a,b** by acidic hydrolysis afford the alcohols **8a,b**, which in the presence of silica gel, rearrange into the quinizarin derivative **10a** and minor amounts of the naphthofuran **11** The rearrangement of **8a,b** with silica gel in the presence of ethanol affords the naphthofuran type products **12** and **15** The thermal rearrangement of alcohols **8a,b** by heating in benzene solution affords a mixture of the rearranged products **10a,b** and the spirocompound **18** Under similar thermal conditions, the alcohol **3** produced the leuconaphthazarin derivative **19** and the spirocompound **20**

INTRODUCTION

We have earlier described[2] the synthesis of Diels-Alder adducts of (*E*)-1-trimethylsilyloxybuta-1,3-diene with quinones bearing electron-withdrawing groups Recently, we have also reported[3,4] on the reactivity of compounds **1** and **2** under acid catalysed conditions These studies indicated that adducts of type **1** (R= COMe, CHO, CO_2Me, COCH=CHPh and NO_2), by treatment with diluted hydrochloric acid in THF solution undergo a facile rearrangement to produce dihydrobenzo[*b*]furans of type **4** in 70-99% yields. Compound **3**, obtained from the acidic hydrolysis of adduct **2**, failed to undergo this rearrangement under the same conditions. We have found, however, that a rearrangement occurred when **3** was subjected to the action of silica gel in chloroform-ethanol solution to give the benzodifuran **5** in 70% yield.



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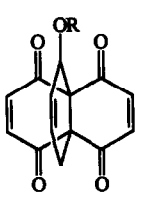
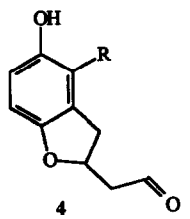


2, R=TMS
3, R=H



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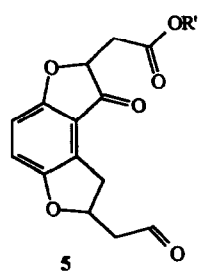

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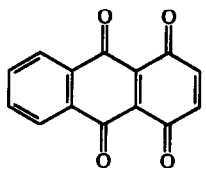
RESULTS AND DISCUSSION

With the aim to explore the scope of the above rearrangement we have also examined the behaviour of the tetracyclic alcohol **8** which could lead to naphthodifuran derivatives. Cycloaddition of (*E*)-1-trimethylsilyloxybuta-1,3-diene with anthradiquinone **6** occurred under mild conditions and afforded a 1 4 diastereomeric mixture of the internal cycloadducts **7a,b** in 96% yield. The high site-selectivity for the attack of the electron-rich diene, which occurs exclusively at the more reactive 4a,9a double bond, was expected on the basis of our results on Diels-Alder reaction of napththodiquinone with (*E*)-1-trimethylsilyloxybuta-1,3-diene[2] and those reported previously[5] with the quinone **6** and 1,3-disubstituted electron-rich dienes The angular structure of the isomers **7a,b** was deduced from the ^{1}H NMR spectrum of the mixture which showed two AB systems (δ 6.57, 6 89 and 6.62, 7.06) assigned to the vinylic protons of both enedione moieties The diastereomers **7a,b** could be separated by chromatography.



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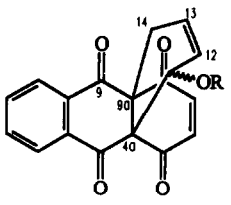
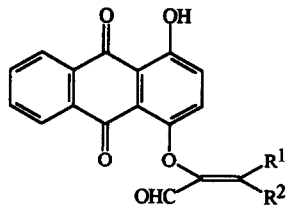


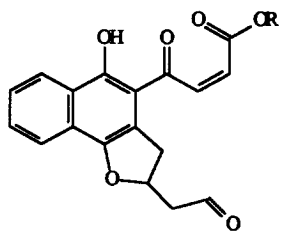
7a, b, R = TMS
8a, b, R = H
9a, b, R = Me



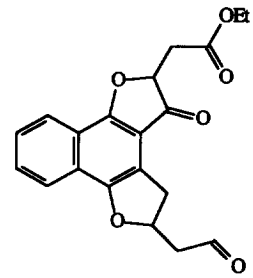
10a, R^1 = CH_3 , R^2 = H
10b, R^1 = H , R^2 = CH_3

Treatment of the **7a,b** mixture with 1.3 N hydrochloric acid in THF resulted only in the hydrolysis of the OTMS group to give a 1.4 mixture of the alcohols **8a,b** in 70% yield In an analogous cycloaddition reaction, anthradiquinone **6** and (*E*)-1-methoxybuta-1,3-diene afforded the expected adduct as a 1.4 diastereomeric mixture **9a,b**, the structure of which was confirmed from the NMR spectrum which was very similar to those of **7a,b**. It is remarkable that the adduct **9a,b** is stable to acidic conditions and all the attempts to produce a rearrangement in the presence of hydrochloric acid led only to recovering of the starting material

Compounds **8a,b** by treatment with 8 N hydrochloric acid in THF solution for 4 days at room temperature gave only unchanged starting material However, when the mixture of alcohols **8a,b** was reacted with silica gel in chloroform (HPLC grade stabilised with *p*-cymene) solution at room temperature a mixture of the rearranged compounds **10a** and **11** were obtained in 85 and 5% yield, respectively



11, R = H
12, R = Et



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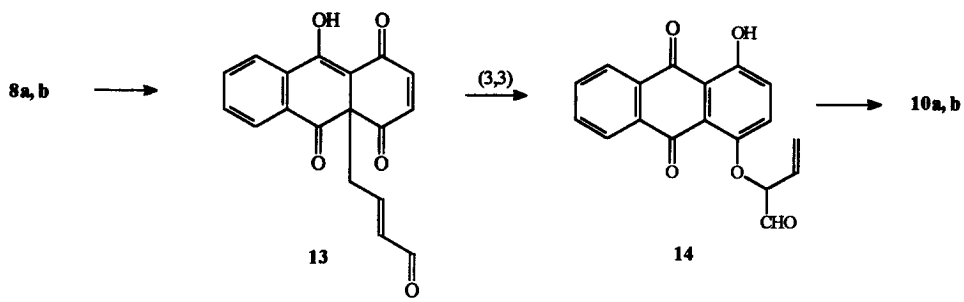
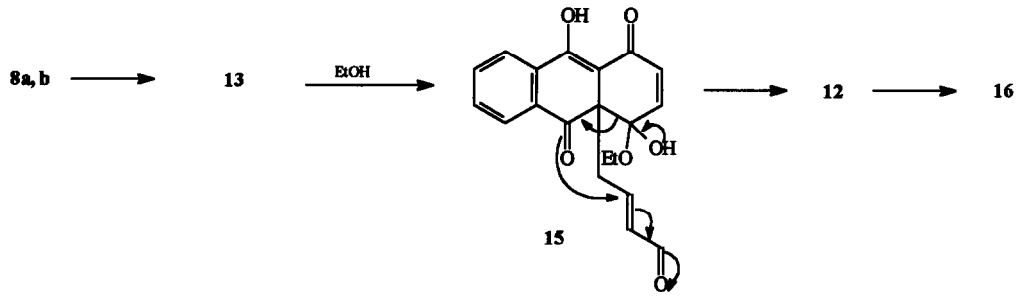
The structure of the quinizarin derivative **10a** was established on the basis of its ^{1}H NMR spectrum, which showed a CHO singlet (δ 9 36), a CH_3 doublet (δ 2.05), a singlet of a hydrogen-bonded OH proton (δ 13 04), and an AB system (δ 7.19 and 7 09, J=9 3 Hz) attributable to the H-2 and H-3 aromatic protons This compound is presumably generated (Scheme I) through a 4a,11 carbon-carbon cleavage in **8a,b**, to give the intermediate **13**, which undergoes a [3,3]-sigmatropic rearrangement similar to those previously reported in related systems[6], followed by a double bond isomerization



Scheme I

The structure of the naphthofuran derivative **11** was deduced from its ^{1}H NMR spectrum, which displayed a hydrogen-bonded OH proton at δ 11 66, a double doublet for the aldehydic proton at δ 9 69 (J=1 3 and 1 6 Hz), two olefinic protons at δ 6 97 and 6 88 in a *cis* arrangement (J=8 8 Hz) and a broad signal of a COOH group at δ 3 58.

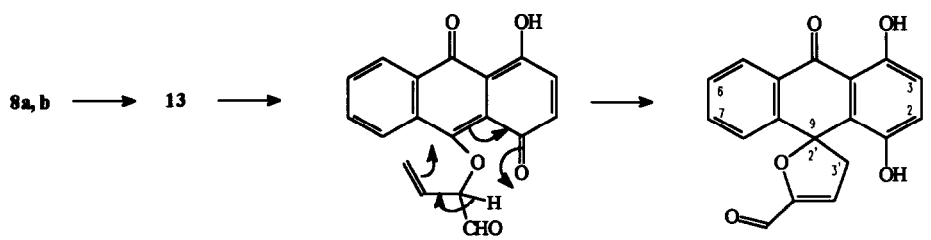
When the alcohols **8a,b** were treated with silica gel in 9 1 chloroform-ethanol solution at room temperature, a mixture of compounds **10a** and **12** was obtained in 25% and 50% yield, respectively. This fact indicated that the presence of ethanol has a noticeable influence upon the reactivity of the alcohol **8**, and presumably facilitates the 4,4a bond fission in the tricyclic intermediate **13** through the formation of the



Scheme II

hemiketal intermediate **15**, as outlined in Scheme II. This assumption was confirmed by conducting the above reaction in 1·1 chloroform-ethanol solution. In this case, compound **10a** was not detected (by TLC and ^{1}H NMR) and the reaction gave a mixture of the rearranged compounds **12** and **16** in 75% and 5% yield, respectively. Compound **16** probably arises from the cyclisation of naphthofuran **12** induced by the silica gel in a manner similar to that observed recently by us starting from the tricyclic alcohol **3**[4]

Taking into account these results we have also investigated the reactivity of the alcohols **8a,b** under thermal conditions without any catalysis, in order to induce a [3,3]- and/or [1,5]-sigmatropic rearrangement, which have precedent in related systems[6]. When the isomeric mixture **8a,b**, was refluxed in benzene for 2 days, it was rearranged to the quinone **10** and the spirocompound **18** in 70% and 10% yield, respectively The major component **10** was isolated as a 9 1 *Z*/*E* mixture (**10a**+**10b**), estimated by integration of the corresponding CH_3 signals at δ 2.05 and 2.12 in the ^{1}H NMR spectrum

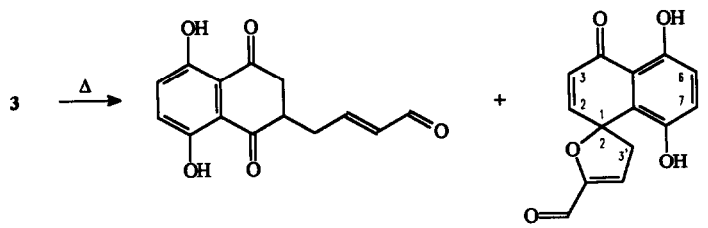


Scheme III

The ^{1}H NMR spectrum of **18** showed one aldehydic proton (δ 9.34), one free (δ 3.86) and one hydrogen-bonded phenolic proton (δ 13 03), and signals of an ABX system (δ 2 83, 3.24, and 6 07),

assigned to the furan ring protons The ^{13}C NMR spectrum of **18** displayed two carbonyl carbons at δ 187 7 and 186 7 and a methylene carbon at δ 44.7, and confirmed the spiro union by the presence of a quaternary aliphatic carbon signal at δ 69 7 The formation of **18** can be rationalised as shown in Scheme III. The intermediate **13** formed from **8a,b** undergoes a [3,3] sigmatropic rearrangement to give the intermediate **17** which cyclizes to the spirocompound **18**

In view of the above results, we also attempted to promote a thermal rearrangement in the tricyclic alcohol **3** by refluxing in benzene solution for 2 days Under these conditions, the leuconaphthazarin derivative **19** and the spirocompound **20** were generated in 70% and 15% yield, respectively (Scheme IV) The leuconaphthazarin structure of **19** was assigned by its ^1H NMR spectrum which showed two hydrogen-bonded OH protons (δ 11.80 and 11.86), two aromatic protons (δ 7 27), five mutually coupled protons (δ 2 74-3 31), one aldehydic proton (δ 9 55) and two olefinic protons (δ 6 21 and 6 86, J=15 7) The structure of **20** was based on its ^1H and ^{13}C NMR spectral data, which were very similar to those of spirocompound **18**.



19 **20**

Scheme IV

In summary, the course of the rearrangement is different in the alcohols **3** and **8** and is strongly dependent on the reaction conditions The rearrangements reported here offer efficient entries to novel furan containing cyclic systems and provide a ready access to compound **19**, which is a promising synthon for the construction of the tetracyclic system of anthracyclinones.

EXPERIMENTAL

M p.s were determined with a Kofler hot-stage apparatus and are uncorrected. Microanalyses were performed with a Heraeus analyzer. IR spectra were recorded on a Perkin-Elmer model 681 grating spectrophotometer as nujol mulls, ν values in cm^{-1} ^1H NMR spectra were determined with either a Varian EM-390, a Bruker AM-200 or a Varian XL-300 spectrometer, in $CDCl_3$ solution, unless otherwise stated ^{13}C NMR were determined with either a Varian XL-300 or a Bruker AM-200 in $CDCl_3$ solution, unless otherwise

stated. Chemical shifts were reported in p p m. (δ) downfield from Me_4Si Mass spectra were determined on a VG-12-250 spectrometer. Silica gel Merck 60 (70- 230 mesh) and DC-Alufolien $60F_{254}$ were normally used for preparative column and analytical TLC respectively

The alcohol **3** was prepared according to the method previously reported[4].

Reaction of Anthracene-1,4,9,10-tetraone (6) with (*E*)-1-Trimethylsilyloxybuta-1,3-diene.

To a solution of the diquinone **6**[7] (2.36 g, 10 mmol) in dichloromethane (60 ml) was added (*E*)-1-trimethylsilyloxybuta-1,3-diene (1.53 g, 10 mmol) and the mixture was allowed to stand at room temperature for 12 h. The solvent was removed under reduced pressure and the crude was triturated with diethyl ether to give 11-trimethylsilyloxy-4a,9a-dihydro-4a,9a-(but-2-eno)anthracene-1,4,9,10-tetraone (**7**) (3 65 g , 96%) as a 1:4 mixture of two diastereomers (determined by ^{1}H NMR) Anal Calcd for $C_{21}H_{20}O_5Si$ C, 66.31, H, 5.26 Found: C, 65.91; H, 5.05% These isomers were separated by flash column chromatography (3 1 petroleum ether-chloroform)

Adduct 7a m p 145-149 °C; ν_{max} 1720, 1710, 1685, 1595, δ_H (300 MHz): -0 34 (9H, s, $OSiMe_3$), 2 14 (1H, d, J 19 0 Hz, 14- H), 3 39 (1H, dd, *J* 19 0, 2 6 Hz, 14-H'), 4.93 (1H, m, 11-H), 5 80- 5 95 (2H, m, 12-H, 13-H), 6 57, 6.89 (2H, AB syst , *J* 10 4 Hz, 2-H, 3-H), 7 64-7.80 (2H, m, 6-H, 7-H), 8 01-8 10 (2H, m, 5-H, 8-H), δ_C (200 MHz) -0.86, 27 26, 62 47, 65 56, 69 31, 125.97, 126 58, 126 94, 133 15, 134.72, 137 44, 138 16, 142 04, 188 98, 191 03, 192 70, 194 86, *m/z* 381 (M^++1), 380 (M^+), 365, 352, 335, 309, 298, 290, 282, 240 (100), 221, 73.

Adduct 7b m p 112-115 °C, ν_{max} 1720, 1710, 1685, 1590, δ_H (300 MHz): -0 02 (9H, s, $OSiMe_3$), 2 04 (1H, d, *J* 19 0 Hz, 14-H), 3 24 (1H, ddd, *J* 19.0, 4.4, 1.4 Hz, 14-H'), 5 09 (1H, d, *J* 4 9 Hz, 11-H), 5.80-5 95 (2H, m, 12-H, 13-H), 6 62, 7 06 (2H, AB syst , *J* 10 4 Hz, 2-H, 3-H), 7.64-7 80 (2H, m, 6-H, 7-H), 8 01-8 10 (2H, m, 5-H, 8-H); δ_C (200 MHz): -0.19, 26 36, 62 15, 65 92, 69 49, 125 66, 127 26, 127 48, 128 06, 131 49, 134 71, 135 01, 135 39, 139 34, 144 72, 189 15, 190 25, 193 47, 193 74, *m/z* 381 (M^++1), 380 (M^+), 365, 352, 335, 319, 298 (100), 291, 282, 73

Reaction of Adducts 7a,b in Acidic Medium.

A solution of the mixture of the isomeric adducts **7a,b** (1.9 g, 5 mmol) in THF-water (9 1, 100 ml) and 1 3 N hydrochloric acid (1 ml) was kept at room temperature for 24 h. The mixture was poured into water and the solution was extracted with chloroform The organic layer was washed with water and dried ($MgSO_4$) The solvent was removed and the crude product was triturated with diethyl ether to give 11-hydroxy-4a,9a-dihydro-4a,9a-(but-2-eno)anthracene-1,4,9,10-tetraone (**8a,b**) (1 08 g, 70%) as a 1 4 mixture of diastereomers (determined by ^{1}H NMR), ν_{max} 3500, 1705, 1675, 1595, δ_H (300 MHz, acetone-d_6) 2 20 (1H, d, *J* 18 0 Hz, 14-H), 3.10 (1H, d, *J* 18 0 Hz, 14-H'), 4 65 (0 2H, d, *J* 4.1 Hz, 11-H), 4 77 (0 8H, d, *J* 4 1 Hz, 11-H), 4 93 (0 2H, br s, OH), 5 02 (0 8H, br s, OH), 5 79-5 99 (2H, m, 12-H, 13-H), 6 75, 7 12 (1 6H, AB syst , *J* 10.5 Hz, 2-H, 3-H), 6 75, 7 03 (0 4H, AB syst , *J* 10 5 Hz, 2-H, 3-H), 7 80-8 10 (4H, m, 5-H,

6-H, 7-H and 8-H); δ_C (200 MHz, acetone-d_6): 27 37, 28.09, 63 57, 63.87, 65 74, 69 90, 126.24, 126 61, 127.36, 127.86, 128.07, 128.25, 128.55, 128.74, 132 66, 134.51, 135 77, 135.95, 136 61, 138 75, 140.81, 142 98, 145.13, 190.43, 192 07, 193.69, 195 97, *m/z* 308 (M^+), 290, 280, 262, 240 (100), 209, 183, 76 Anal. Calcd for $C_{18}H_{12}O_5$ · C, 70.13; H, 3.89. Found: C, 69 94, H, 3.90%.

Attempted Cleavage of the Alcohols 8a,b in Hydrochloric Acid.

To a solution of the alcohols **8a,b** (77 mg, 0.25 mmol) in THF-water (9 1, 5 ml) was added 8 N hydrochloric acid (5 drops) and the mixture was kept at room temperature for 4 days After the usual work-up, the residue was shown to be recovered alcohol **8a,b** (by ^{1}H NMR)

Reaction of Anthracene-1,4,9,10-tetraone (6) with (*E*)-1- Methoxybuta-1,3-diene

To a solution of the diquinone **6** (1 19 g, 5 mmol) in dichloromethane (60 ml) was added (*E*)-1-methoxybuta-1,3-diene (462 mg, 5 5 mmol) and the mixture was allowed to stand at room temperature for 12 h The solvent was removed under reduced pressure and the crude was triturated with diethyl ether to give the adduct **9a,b** (1 53 g, 95%), as a 1 4 mixture of two diastereomers (determined by ^{1}H NMR), ν_{max} 1740, 1710, 1690, 1680, δ_H (300 MHz) 2.06 (0 8 H, d, *J* 19 6, 14-H), 2 15 (0.2 H, d, *J* 19 5, 14-H), 3.01 (0 6 H, s, OMe) 3 23 (2 4 H, s, OMe), 3 25 (0.8 H, ddd, *J* 19 6, 4 3, 1.9 Hz, 14-H'), 3 39 (0.2 H, ddd, *J* 19 5, 4 5, 1 6 Hz, 14-H'), 4 55 (0 2 H, dd, *J* 4 6, 0 8 Hz, 11-H), 4.69 (0 8 H, dd, *J* 4.7, 0 5 Hz, 11-H), 5.90-6.20 (2H, m, 12-H, 13-H), 6 58, 6 91 (0 4 H, AB syst , *J* 10 2, 12-H, 13-H), 6.67, 7.06 (1 6 H, AB syst., *J* 10 3 Hz, 12-H, 13-H), 7 66-7 84 (2H, m, 6H, 7H), 8 04-8 11 (2H, m, 5H, 8-H), δ_C (200 MHz): 26.73, 27 59, 57 05, 62 41, 68 58, 73 20, 123 92, 124 13, 126 86, 127 21, 127.54, 127 72, 128 18, 131 55, 133 35, 134 83, 135 54, 137 46, 139 46, 141 98, 144 51, 188 87, 190 36, 190 50, 193 28, 193.30, *m/z* 322 (M^+), 294, 277, 240 (100), 225, 209, 190, 152, 91 Anal Calcd for $C_{19}H_{14}O_5$: C, 70 80, H, 4.34. Found C, 71 00, H, 4 43

Attempted Cleavage of Adducts 9a,b

To a solution of the adduct **9a,b** (80 mg, 0.25 mmol) in THF-water (9·1, 20 ml) was added 1.3 N hydrochloric acid (6 drops) and the solution was kept at room temperature for 6 days. After the usual work-up, the residue was shown to be recovered adduct (by ^{1}H NMR) Attempts of cleavage effected by using 8.5 N hydrochloric acid (3 drops) at room temperature for 3 days were also unsuccessful.

Cleavage of 11-Hydroxy-4a,9a-dihydro-4a,9a-(but-2-eno)anthracene-1,4,9,10-tetraone (8a,b)

Method A.

A mixture of the isomeric alcohols **8a,b** (200 mg, 0 65 mmol), silica gel (3 g, Merck 70-230 mesh) and chloroform stabilised with amylene (100 ml) was vigorously stirred at room temperature for 10 days. The resulting mixture was filtered and the solvent removed The crude mixture was separated by flash

chromatography. Elution with chloroform afforded the *O*-substituted quinizarin **10a** (170 mg, 85%); m.p 184-185 °C; ν_{max}: 1700, 1680, 1650, 1600; δ_H (300 MHz) 2 05 (3H, d, *J* 7.1 Hz, Me), 6.52 (1H, q, 7 1 Hz, =CH), 7 19, 7.08 (2H, AB syst , *J* 9 3 Hz, 2-H, 3-H), 7.79 (2H, m, 6-H, 7-H), 8.26 (2H, m, 5-H, 8-H), 9.36 (1H, s, CHO), 13.04 (1H, s, OH), δ_C (200 MHz). 17 17, 115 70, 119 85, 125 73, 126.42, 126 54, 127.30, 132.28, 133 45, 134 04, 134.73, 136.95, 150.29, 151 49, 158 84, 181.06, 186.08, 188 68, *m/z* 310 (M^++2), 308 (M^+), 279, 265, 263, 251 (100), 240, 236, 224, 177, 149, 138, 77. Anal Calcd. for $C_{18}H_{12}O_5$ C, 70 13, H, 3 89 Found C, 69.99, H, 4 02. Further elution with ethyl acetate afforded compound **11** (16 mg, 5%), m.p 177-182 °C, ν_{max}: 3432, 2925, 2853, 1718, 1628 δ_H (300 MHz). 1.96 (1H, dd, *J* 16.9, 7.3 Hz, 3-H), 2.47 (1H, dd, *J* 16 9, *J* 9 1 Hz, 3-H'), 2 54 (1H, ddd, *J* 17.2, 5 3, 1 3, 1'-H), 2.78 (1H, ddd, *J* 17.2, 7 3, 1 6 Hz, 1'-H'), 3.58 (1H, br s, OH), 4 93 (1H, m, 2-H), 6 97, 6 88 (2H, AB syst , *J* 8.8, =CH), 7.32 (1H, dd, *J* 6.8, 1.1 Hz, 9-H), 7.61 (1H, dt, *J* 7.7, 7.6, 1 4 Hz, 7-H), 7.71 (1H, dt, *J* 7 5, 7 4, 1 3 Hz, 8-H), 8.13 (1H, dd, *J* 8.3, 1 1 Hz, 6-H), 9.69 (1H, t, *J* 1 3, 1 6 Hz, CHO), 11.66 (1H, br s, OH). *m/z* 326 (M^+), 281, 265, 237, 149, 83 (100).

Method B

A mixture of the isomeric alcohols **8a,b** (308 mg, 1 mmol), silica gel (4 g, Merck 70-230 mesh), 95% ethanol (10 ml) and chloroform (90 ml) was vigorously stirred at room temperature for 10 days. The resulting mixture was filtered an the solvent removed The crude mixture was separated by flash chromatography (chloroform) to afford the *O*-substituted quinizarin **10a** (77 mg, 25%) and compound **12** (177 mg, 50%), m p 131-135 °C; ν_{max} : 1725, 1705, 1645, 1590; δ_H (300 MHz) 1.18 (3H, t, *J* 7 2, Me), 1.96 (1H, dd, *J* 16 9, 7.3 Hz, 3-H), 2.50 (2H, m, 3-H', 1'-H), 2.77 (1H, ddd, *J* 17.2, 7.2, 1 9 Hz, 3-H'), 4.22 (1H, q, *J* 7 2 Hz, OCH_2), 4.92 (1H, m, 2-H), 6.88, 6.96 (2H, AB syst., *J* 8.9, =CH), 7 32 (1H, dd, *J* 7.3, 1.4 Hz, 9-H), 7.59 (1H, dt, *J* 7.3, 7 4, 1.4 Hz, 8-H), 7.67 (1H, dt, *J* 7 6, 7 4, 1.4 Hz, 7-H), 8.09 (1H, dd, *J* 7.6, 1.4 Hz, 6-H), 9.70 (1H, t, *J* 1.9, 1.2 Hz, CHO), 11.73 (1H, s, OH), δ_C (200 MHz): 13.63, 36 86, 49 14, 61.88, 77 16, 117 39, 118 02, 118 39, 125.79, 126.04, 128.11, 129.94, 130.66, 132 96, 142 34, 151.89, 157 49, 165 49, 199 74, 201.71, *m/z* 354 (M^+), 280, 265, 250, 240 (100), 180, 152, 149, 139, 97, 71

Method C.

A mixture of the isomeric alcohols **8a,b** (308 mg, 1 mmol), silica gel (4 g, Merck 70-230 mesh), 95% ethanol (50 ml) and chloroform (50 ml) was vigorously stirred at room temperature for 10 days. The resulting mixture was filtered an the solvent removed. The crude mixture was separated by flash chromatography (chloroform) to afford compounds **12** (265 mg, 75%) and **16** (17 mg, 5%), ν_{max} 1740, 1710, 1645, 1600, δ_H (300 MHz): 1 27 (3H, t, *J* 7.2, Me), 2 75-3 0 (2H, m, 1'-H, 1''-H), 3 0-3 33 (3H, m, 1'-H, 1''-H', 4-H), 3.58-4.0 (1H, m, 4-H'), 4.12-4.25 (2H, m, OCH_2), 5 0-5 13 (1H, m, 5-H), 5.42-5 60 (1H, m, 2-H), 7 54 (1H, t, *J* 8.1, Hz, arom.), 7 70 (1H, t, *J* 8.1, Hz, arom), 7 92 (1H, d, *J* 8 1 Hz, arom.), 8 19 (1H, d, *J* 8 1 Hz, arom), 9.92 (1H, t, *J* 1 2 Hz, CHO).

Thermal Rearrangement of 9-Hydroxy-4a,8a-dihydro-4a,8a(but-2-eno)-naphthalene-1,4,5,8-tetraone (3)

A solution of alcohol **3** (2.58 mg, 1 mmol) in benzene (30 ml) was heated under reflux for 48 h The solvent was removed and the crude mixture was separated by flash chromatography (chloroform) to afford the leuconaphthazarin **19** (172 mg, 67%), ν_{max} (film). 1720, 1690, 1660; δ_H (300 MHz). 2 74 (1H, m, 1'-H), 2 98 (3H, m, 1'-H', 3-H, 3-H'), 3 31 (1H, m, 2-H), 6 21 (1H, dd, *J* 15 7, 7 7 Hz, 3'-H), 6 86 (1H, m, 2'-H), 7 27 (2H, s, 6-H, 7-H), 9.55 (1H, d, *J* 7 7 Hz, CHO), 11 80 (s, 1H, OH), 11 86 (1H, s, OH), δ_C (200 MHz) 32 94, 41 53, 44 76, 113 85, 114 24, 128.78, 135 57, 152 39, 155 24, 155 44, 193 01, 200 18, 201.57, *m/z* 260 (M^+), 242, 204, 189, 149, 111, 97, 83, 69, 57 (100), 43. Anal. Calcd for $C_{14}H_{12}O_5$· C, 64 61, H, 4 62. Found C, 64.70, H, 4 75, and spirocompound **20** (34 mg, 15%), m p 130 °C, ν_{max} 3400, 1670, 1660, 1620, δ_H (300 MHz) 2.74 (1H, dd, *J* 19 3, 2 9 Hz, 3'-H), 2.99 (1H, dd, *J* 19 3, 6.2 Hz, 3'-H), 3 48 (1H, br s, OH), 6 01 (1H, dd, *J* 6 2, 2 9 Hz, 4'-H), 6 36 (1H, d, *J* 10 2 Hz, 3-H), 6 92 (1H, d, *J* 10 2, 2-H), 6 93, 7 38 (2H, AB syst , *J* 9 1 Hz, 6-H, 7-H), 9 28 (1H, s, CHO), 12.39 (1H, s, OH); δ_C (300 MHz) 39 75, 68 61, 112.46, 118 97, 125 26, 127.13, 130 13, 134.40, 147 59, 151 13, 151.63, 159.77, 186.74, 189 02, *m/z* 258 (M^+), 203, 149, 111, 97, 69, 55 (100).

Thermal rearrangement of 11-hydroxy-4a,9a-dihydro-4a,9a-(but-2-eno)anthracene-1,4,9, 10-tetraone (8a,b)

A solution of the isomeric alcohols **8a,b** (308 mg, 1 mmol) in benzene (30 ml) was heated under reflux for 48 h. The solvent was removed and the crude mixture was separated by flash chromatography (chloroform) to afford the *O*-substituted quinizarin **10a,b** as a 9·1 mixture of *E/Z* isomers (215 mg, 70%), δ_H (300 MHz) 2.05 (2 7H, d, *J* 7 1 Hz, Me **10a**), 2 12 (0 3H, d, *J* 7 9 Hz, Me **10b**), 5.93 (0.1H, q, *J* 7 9, =CH **10b**), 6 52 (0 9H, q, 7 1 Hz, =CH **10a**), 7 19, 7 08 (1 8H, AB syst , *J* 9 3, 2-H, 3-H **10a**), 7 27, 7 30 (0.2H, AB syst , *J* 9 51 Hz, 2-H, 3-H, **10b**), 7 79 (2H, m, 6-H, 7-H, **10a,b**), 8 26 (2H, m, 5-H, 8-H, **10a,b**), 9 36 (0 9H, s, CHO, **10a**), 10 04 (0 1H, s, CHO, **10b**), 13 04 (0 9H, s, OH, **10a**), 13 09 (0 1H, s, OH, **10b**), and spirocompound **18** (28 mg, 10%), m p 150 °C, ν_{max} . 3430, 1700, 1655, 1640, 1600, δ_H (300 MHz) 2 83 (1H, dd, *J* 19 8, 2.7 Hz, 3'-H), 3.24 (1H, dd, *J* 19 8, 5.9 Hz, 3'-H'), 3 86 (1H, s, OH), 6.07 (1H, dd, *J* 5 9, 2 7 Hz, 4'-H), 6 99, 7 46 (2H, AB system, *J* 8 9 Hz, 2-H, 3-H), 7 56 (1H, t, *J* 7 8, 7.5 Hz, 6-H or 7-H), 7 78 (1H, t, *J* 7 8, 7 5 Hz, 7-H or 6-H), 7 95 (1H, d, 7.8 Hz, 5-H), 8 31 (1H, d, *J* 7 8, 8-H), 9 34 (1H, s, CHO), 13 03 (1H, s, OH); δ_C (300 MHz) 44 66, 69 65, 112 69, 118 87, 126 72, 126 82, 127 37, 128 19, 128.99, 130 80, 135 14, 135 48, 146 01, 147 96, 151.91, 160 86, 186 65, 187 73, *m/z* 308 (M^+), 279, 253, 236, 149 (100), 97, 57, 55, 43

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