APPROACH TO THE SYNTHESIS OF 1,5-DIAZAANTHRAQUINONES BY DIELS-ALDER REACTIONS OF QUINOLINE-5,8-DIONES

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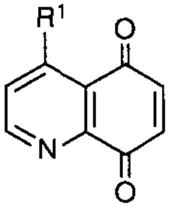
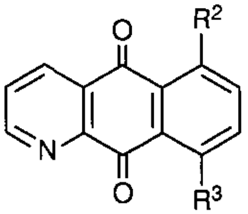
Abstract- 9-Hydroxy- and 6-hydroxybenzo[*g*]quinoline-5,10-dione (**18**) and (**22**) have been obtained through the selective Diels-Alder reaction of 1-trimethylsilyloxy-1,3-butadiene (**8**) with quinoline-5,8-dione (**2**) and *tetrahydroquinoline-5,8-dione* (**7**) *respectively. The treatment of quinone* (**2**) with 1-dimethylamino-1-aza-1,3-butadiene (**9**) affords a mixture of the diazaanthraquinones (**23**) and (**24**) in a 1:3.6 ratio. The synthesis of 1,5-diazaanthraquinone (**26**) *via* the reaction of quinone (**7**) with azadiene (**9**) is also described.

The Diels-Alder reaction of quinoline-5,8-diones with dienes[1] and azadienes[2] has been successfully used to synthesize heterotricyclicquinones. Ohgaki *et al.*[3] studied the Diels-Alder reaction of **1** with piperylene and isoprene and the effect of a Lewis acid on the selectivity of the cycloaddition. They also used more polar dienes such as 1-acetoxy-, 1-methoxy- and 1-trimethylsilyloxy-1,3-butadiene without describing the selectivity of the reaction.

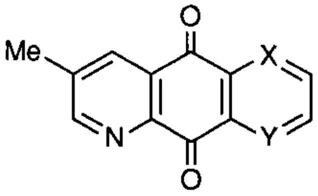
Potts *et al.*[4a] have demonstrated that the electron-withdrawing effect of the quinoline nitrogen atom provides control of the regiochemistry of the reaction of quinoline-5,8-dione (**1**) with 1-methoxy-1,3-cyclohexadiene that afforded 9-methoxybenzo[*g*]quinoline-5,10-dione (**3**) and 6-*methoxybenzo[g]quinoline*-5,10-*dione* (**4**). The *regioisomers* (**3**) and (**4**) were obtained in a 8.9:1 ratio, and they confirmed their structural assignement by synthesis of both isomers using heteroatom-directed lithiation procedures. They also found that the reaction of **1** with 1-dimethylamino-3-methyl-1-aza-1,3-butadiene (**10**) is more selective and gave, regiospecifically, the 1,8-diazaanthraquinone (**5**) in 74% yield.[4c] However, there is another report stating that in the above reaction the compound (**5**) is generated along with 1,5-diazaanthraquinone (**6**), the latter one being obtained in up to 12% yield.[5] The effects of ultrasound in the reaction of quinoline-5,8-diones with 1-aza-1,3-dienes were studied recently and produce an increase of the reaction rate, but it has no significant influence on the regioselectivity of the cycloaddition.[6]



1 $R^1 = H$
2 $R^1 = Cl$

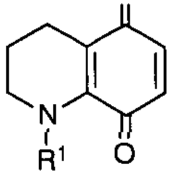


3 $R^2 = H, R^3 = OMe$
4 $R^2 = OMe, R^3 = H$

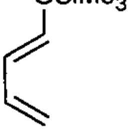


5 X = C, Y = N
6 X = N, Y = C

In these reactions the electron-withdrawing effect of the nitrogen atom of the quinoline-5,8-dione (**1**) makes the C-8 carbonyl group more electron-defficient directing the attack of the more nucleophilic end of the 1-aza-1,3-diene to the C-6 of the dienophile, and the main product is a 1,8-diazaanthraquinone. It would be useful to apply this procedure to a suitable substrate, for the regioselective synthesis of the 1,5-diazaanthraquinone system which is the basic skeleton of several polycyclic aromatic alkaloids of great interest due to their biological activities.[7] With this purpose we chose the quinolinequinone (**2**) and tetrahydroquinolinequinone (**7**) expecting that the chlorine atom or the ethoxycarbonyl group would make the C-5 carbonyl group more electron-defficient directing the attack of the more nucleophilic terminus of the diene to C-7 in dienophiles (**2**) and (**7**) respectively.



7 $R^1 = CO_2Et$



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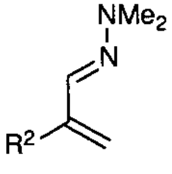


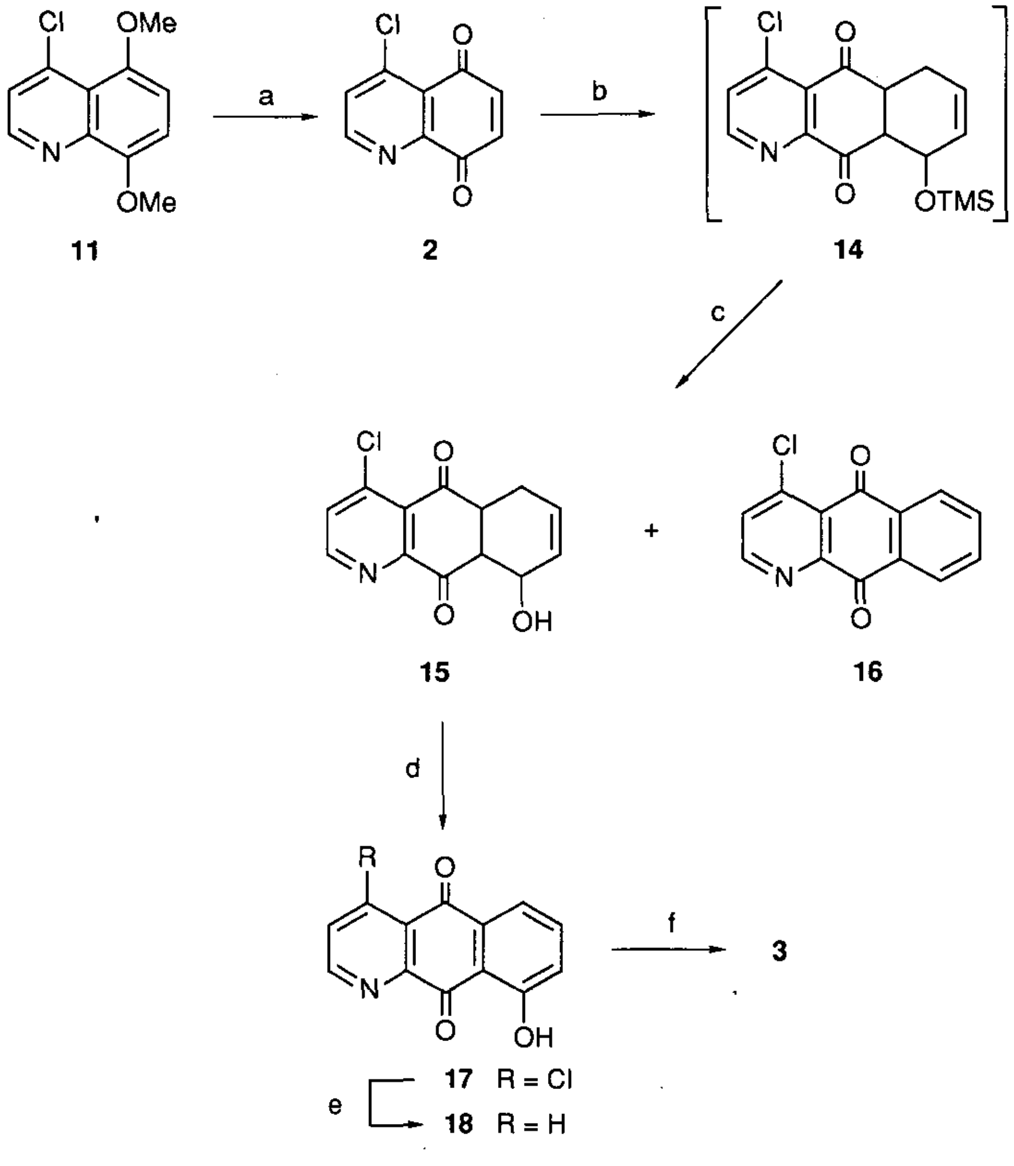
9 $R^2 = H$
10 $R^2 = Me$

In connnection with our work on the synthesis of heterocyclic quinones,[8] we now wish to report the study of the regiochemistry of the Diels-Alder reaction of quinoline-5,8-diones (**2**) and (**7**) with 1-trimethylsilyloxy-1,3-butadiene (**8**) and 1-dimethylamino-1-aza-1,3-butadiene (**9**). Both dienes were selected to facilitate the identification process of the aromatic structures resulting from the corresponding cycloadducts.

The 4-chloroquinoline-5,8-dione (**2**) is readily available and was obtained in 91% yield by oxidation of 4-chloro-5,8-dimethoxyquinoline (**11**) with cerium (IV) ammonium nitrate.[9] For the synthesis of quinone (**7**), the quinoline (**11**) was converted by hydrogenation over Raney nickel W-2 to the known 1,2,3,4-tetrahydro-5,8-dimethoxyquinoline (**12**)[10] in 89% yield. Protection of the amino group of compound (**12**) with ethyl chloroformate-sodium hydride in tetrahydrofuran gave after column chromatography, the carbamate (**13**) (89%). Then the oxidation of (**13**) using the method of Rapoport[9] (AgO in tetrahydrofuran in the presence of nitric acid) provided quinone (**7**) (54%).

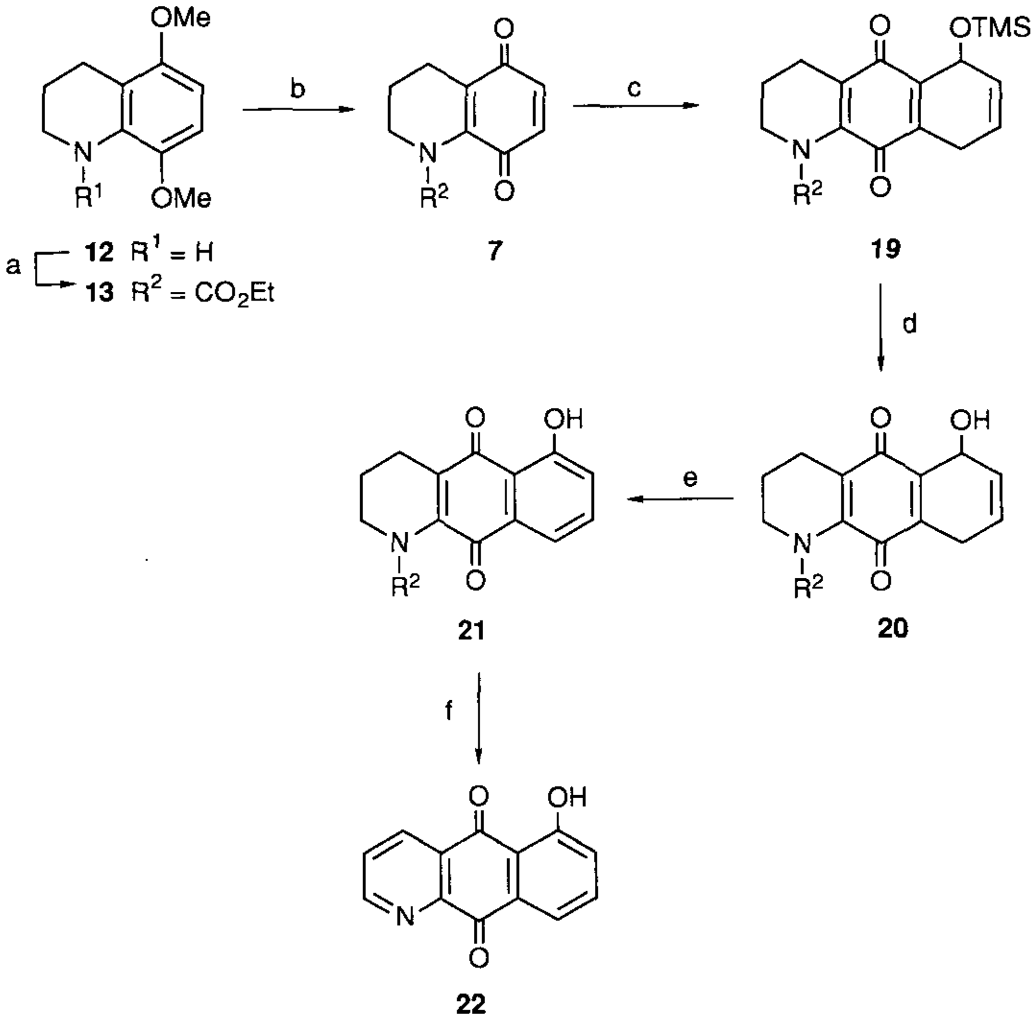
The reaction of quinoline-5,8-dione (**2**) with diene (**8**) in methylene chloride at room temperature for 3 days gave adduct (**14**) whose ^{1}H-nmr spectra showed the presence of only one signal for the trimethylsilyloxy group. Because this adduct was unstable, it was inmediately hydrolized with 1N HCl to give the unsaturated alcohol (**15**) and the elimination-oxidation product (**16**) in 59% and 17% yields, respectively. Our initial structural assignment was based on the described regiochemistry for the cycloaddition of quinoline-5,8-dione (**1**) with 1-methoxy-1,3-cyclohexadiene, and it was confirmed by transformation of the unsaturated alcohol (**15**) into the known 9-methoxybenzo[*g*]quinoline-5,10-dione (**3**).

Oxidation of compound (**15**) with PCC gave the phenol (**17**) in 73% yield. When compound (**17**) was treated with hydrogen in the presence of palladium on activated carbon in basic methanol, the 9-hydroxybenzo[*g*]quinoline-5,10-dione (**18**) was obtained (66%). Reaction of the latter with methyl iodide and silver(I) oxide furnished methoxyquinone (**3**) in good yield (84%). The preceding results showed that in the Diels-Alder reaction of quinoline-5,8-dione (**2**) and 1-trimethylsilyloxy-1,3-butadiene (**8**), the more nucleophilic terminus of the diene adds to the C-6 of the dienophile, and therefore quinoline-5,8-diones (**1**) and (**2**) have the same selectivity in their cycloaddition reaction with polar 1,3-dienes.



Reagents: (a) $(NH_4)_2Ce(NO_3)_6$, MeCN; (b) **8**, CH_2Cl_2; (c) 1N HCl, THF-H_2O; (d) PCC, CH_2Cl_2; (e) H_2, 10% Pd-C, KOH, MeOH; (f) MeI, Ag_2O, CH_2Cl_2.

Scheme I



Reagents: (a) NaH, THF; $ClCO_2Et$; (b) AgO, THF-6N HNO_3; (c) **8**, CH_2Cl_2; (d) 1N HCl, THF-H_2O; (e) PCC, CH_2Cl_2; (f) KOH, MeOH; then DDQ, benzene.

Scheme II

The treatment of tetrahydroquinoline-5,8-dione (**7**) with 1-trimethylsilyloxy-1,3-butadiene (**8**) in dichloromethane at room temperature for 4 days gave adduct (**19**) in almost quantitative yield. Deprotection of the silyl ether (**19**) and oxidation of the resulting unsaturated alcohol (**20**) furnished hydroxyquinone (**21**) in 50% yield (two steps). Removal of the ethoxycarbonyl protecting group of carbamate (**21**) with potassium hydroxide and oxidation with DDQ afforded

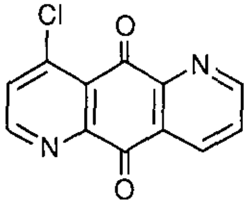
6-hydroxybenzo[*g*]quinoline-5,10-dione (**22**) in 50% yield. The ^{1}H-nmr data of isomers (**18**) and (**22**) showed that the hydrogen-bonded OH proton of **18** (δ 12.50 ppm) resonates more downfield than compound (**22**) (δ 12.33 ppm). This was attributed to the influence of the nitrogen atom, making C-10 the more electron-deficient carbonyl group. These results demonstrated the reverse selectivity of the quinoline-5,8-diones (**2**) and (**7**) in the cycloaddition reaction with 1-trimethylsilyloxy-1,3-butadiene (**8**).

We next examined the reaction of quinoline-5,8-dione (**2**) with 1-dimethylamino-1-aza-1,3-butadiene (**9**). According to described procedures, addition of silica gel and an oxidant agent is necessary to accelerate the aromatization-oxidation process of the corresponding adducts.[2] Under these conditions we obtained a mixture of compounds that was separated by column chromatography yielding 1,5-diazaanthraquinone (**23**) and 1,8-diazaanthraquinone (**24**) in 12% and 43% yield respectively. Because the ^{1}H-nmr spectra of isomers (**23**) and (**24**) are very similar, the structure of each isomer is inferred by comparison of the corresponding ir spectra. Considering the known effect of the nitrogen atom of the pyridine ring, that increases the wave number of the neighbour carbonyl group,[4,5] we proposed for the 1,8-diazaanthraquinone the structure (**24**) because it showed two C=O stretching vibrations in the ir spectra at 1690 and 1670 cm^{-1}, while 1,5-diazaanthraquinone (**23**), exhibited only one carbonyl band at 1690 cm^{-1}.

Finally, the reaction of tetrahydroquinoline-5,8-dione (**7**) with 1-dimethylamino-1-aza-1,3-butadiene (**9**) afforded diazaquinone (**25**) (52%), whose structure was determined by transformation into the corresponding aromatic diazaquinone (**26**) in 69% yield, through deprotection of the amino group and oxidation with DDQ. The symmetry of 1,5-diazaanthraquinone (**26**) was deduced from its ir and ^{13}C-nmr spectra that showed only one band at 1690 cm^{-1} and one signal at δ 181.0 ppm for a carbonyl group respectively.

In the Diels-Alder reaction of the 4-chloroquinoline-5,8-dione (**2**) with the 1-dimethylamino-1-aza-1,3-butadiene (**9**) the main product is the 1,8-diazaanthraquinone, so the chlorine atom in quinone (**2**) has no significant effect over the selectivity of this reaction. However, in the tetrahydroquinoline-5,8-dione (**7**), the electron-withdrawing effect of the ethoxycarbonyl group, in agreement with our reasoning, produces a change in the selectivity of the reaction with polar

1,3-dienes and 1-aza-1,3-dienes. Considering the high selectivity of the cycloadditions reported here, we think that tetrahydroquinoline-5,8-dione (**7**) *is valuable precursor to synthesise aza- and* 1,5-diazaanthraquinones through regiocontroled cycloaddition reactions. A different strategy, starting from aminoquinolinequinones to obtain 1,5- and 1,8-diazaanthraquinones was reported recently.[13]



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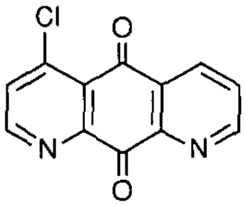

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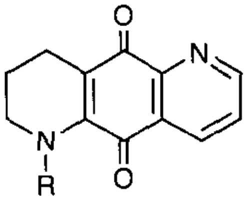
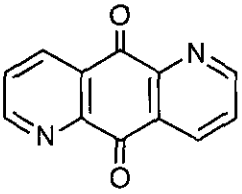


25 R = CO_2Et



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EXPERIMENTAL

Melting points were determined with a Kofler hot-stage apparatus and are not corrected. Ir spectra were obtained on a Perkin-Elmer Model 1310 spectrophotometer. Nmr spectra (^1H and ^{13}C) were recorded on a Bruker AM-200 spectrometer, using tetramethylsilane as internal reference, and coupling constants are given in Hz. Column chromatography was performed on Merck *silica gel 60 (70-230 mesh). Elemental analyses* were performed at the Instituto de Química Orgánica General (CSIC), Madrid, Spain.

1,2,3,4-Tetrahydro-5,-8-*dimethoxyquinoline* (12)

A mixture of the 4-chloro-5,8-dimethoxyquinoline (**11**)[9] (2.5 g, 11.2 mmol) and triethylamine (1.6 ml) in ethanol (70 ml) was hydrogenated using Raney nickel W-2 (0.25 g) as catalyst at room temperature over 12 h. The suspension was filtered and the filtrate was evaporated under reduced pressure. The residue was purified by column chromatography *with dichloromethane* as eluent to give compound (**12**) (1.91 g, 88.4%) as an oil. The spectral data were previously described.[10]

N-Carboethoxy-1,2,3,4-tetrahydro-5,8-dimethoxyquinoline (13)

A solution of amine (**12**) (1.1 g, 5.7 mmol) in dry THF (10 ml) was added dropwise to a stirred suspension of NaH (80% dispersion in oil, 690 mg, 23 mmol) in dry THF (20 ml). After 1 h ethyl chloroformate (0.8 ml, 8.4 mmol) was added and the mixture was stirred for 8 days at room temperature. The reaction mixture was cooled to 0 °C and was quenched with cold water (40 ml). The aqueous layer was extracted with ethyl acetate (3x40 ml). The combined extracts were dried ($MgSO_4$) and evaporated and the residue was purified by column chromatography on silica gel with dichloromethane to give compound (**13**). (1.34 g, 88.7%). Recrystallization from cyclohexane gave needles, mp 109-110 °C. Anal. Calcd for $C_{14}H_{19}NO_4$: C, 63.4; H, 7.2; N, 5.3. Found: C, 63.6; H, 7.3; N, 5.3; ir ν_{max} (KBr): 1680 (C=O) cm^{-1}; ^1H-nmr δ ($CDCl_3$): 1.25 (3 H, t, J 7.1, CH_3), 1.94 (2 H, q, J 6.4, $CH_2CH_2CH_2$), 2.71 (2 H, t, J 6.6, CH_2Ar), 3.44 (2 H, m, CH_2N), 3.79 (3 H, s, CH_3O), 3.80 (3 H, s, CH_3O); 4.15-4.20 (2 H, m, CH_2O), 6.63 (1 H, d, J 8.9, 6-H), 6.73 (1 H, d, J 8.9, 7-H); ^{13}C-nmr δ ($CDCl_3$): 14.6, 20.7, 23.3, 44.5, 55.7, 55.9, 61.8, 106.4, 108.7, 122.0, 129.5, 147.8, 150.9, 155.5.

N-Carboethoxy-1,2,3,4,5,8-hexahydroquinoline-5,8-dione (7)

To a stirred suspension of carbamate (**13**) (250 mg, 0.94 mmol), AgO (470 mg, 3.8 mmol) in THF (10 ml) was added in one portion 6N HNO_3 (1.3 ml). After being stirred for 5 min, the mixture was quenched with water (20 ml) and extracted with CH_2Cl_2 (3x20 ml). The combined extracts were dried ($MgSO_4$) and evaporated to give a yellow oil which was purified by column chromatography on silica gel (CH_2Cl_2) to afford compound (**7**) in 54% yield (120 mg) as an oil. Anal. Calcd for $C_{12}H_{13}NO_4$: C, 61.3; H, 5.6; N, 5.95. Found: C, 61.5; H, 5.7; N, 5.9; ir ν_{max} (KBr): 1710, 1660 and 1640 (C=O) cm^{-1}; ^1H-nmr δ ($CDCl_3$) : 1.25 (3 H, t, J 7.1, CH_3), 1.92 (2 H, m, $CH_2CH_2CH_2$), 2.53 (2 H, t, J 6.7, CH_2C=), 3.67 (2 H, t, J 5.4, CH_2N), 4.19 (2 H, q, J 7.1, CH_2O) 6.69 (1 H, d, J 10.2, 7-H), 6.76 (1 H, d, J 10.2, 6-H); ^{13}C-nmr δ ($CDCl_3$): 14.1, 20.7, 21.9, 44.6, 63.0, 130.0, 135.8, 136.1, 142.9, 154.5, 181.0, 186.0.

Reaction of quinone (2) with 1-trimethylsilyloxy-1,3-butadiene (8)

To a stirred solution of quinone (**2**) (880 mg, 4.6 mmol) in dichloromethane (80 ml) was slowly added 1-trimethylsilyloxy-1,3-butadiene (**8**) (1.2 ml, 6.9 mmol) *via* a syringe, and the mixture was left at room temperature for 3 days. After evaporation of the solvent, the crude adduct (**14**) was dissolved in THF-H_2O (9:1, 130 ml) and 1 N HCl (6.3 ml) was added dropwise at 0 °C and the mixture was stirred for 2 h at the same temperature. The reaction mixture was partitioned between chloroform and water (1:1, 150 ml), and the organic layer was separated. The aqueous layer was extracted with chloroform (2x75 ml) and the combined organic phases were dried over $MgSO_4$ and concentrated to give a solid which after being washed with dichloromethane-light petroleum (bp 40-60 °C) (4:1, 2x20 ml) furnished the alcohol (**15**) (705 mg, 59%). Concentration of the mother liquor and purification of the residue by column chromatography on silica gel eluting with dichloromethane gave compound (**16**) (188 mg, 17%).

4-Chloro-9-hydroxy-5,5a,6,7,8,9,9a,10-octahydrobenzo[*g*]quinoline-5,10-dione (15)

mp 150 °C (decomp.) (from benzene). Anal. Calcd for $C_{13}H_{10}NO_3Cl$: C, 59.2; H, 3.8; N, 5.3; Cl, 13.45. Found: C, 59.3; H, 3.8; N, 5.35; Cl, 13.4; ir ν_{max} (KBr): 3400 (OH), 1690 (C=O) cm^{-1}; ^1H-nmr δ [$(CD_3)_2SO$]: 2.00-2.15 (1 H, m, 6a-H); 2.79 (1 H, dd, J 18.6, 4.7, 6-H), 3.27 (1 H, dd, J 6.0, 4.3, 9a-H), 3.81 (1 H, t, J 6.2, 5a-H), 4.20-4.28 (1 H, m, 9-H), 5.22 (1 H, d, J 3.5, OH), 5.7-5.9 (2 H, m, 7-H and 8-H), 7.87 (1 H, d, J 5.2, 3-H), 8.82 (1 H, d, J 5.2, 2-H); ^{13}C-nmr δ [$(CD_3)_2SO$]: 22.8, 44.6, 52.0, 65.5, 126.8, 129.4, 130.2, 131.3, 143.9, 152.7, 153.0, 194.1, 195.5.

4-Chloro-5,10-dihydrobenzo[*g*]quinoline-5,10-dione (16)

mp 215-216 °C (from benzene). Anal. Calcd for $C_{13}H_6NO_2Cl$: C, 64.1; H, 2.5; N, 5.75; Cl, 14.55. Found: C, 64.1; H, 2.3; N, 5.8; Cl, 14.6; ir ν_{max} (KBr): 1680 and 1660 (C=O) cm^{-1}; ^1H-nmr δ ($CDCl_3$): 7.78 (1 H, d, J 5.1, 3-H), 7.84-7.95 (2 H, m, 7-H and 8-H), 8.96 (1 H, d, J 5.1, 2-H); ^{13}C-nmr δ ($CDCl_3$): 127.4, 127.6, 131.0, 132.2, 133.6, 134.6, 135.0, 145.7, 151.0, 153.7, 180.6, 181.3.

4-Chloro-5,10-dihydro-9-hydroxybenzo[*g*]quinoline-5,10-dione (17)

To a stirred suspension of PCC (500 mg, 2.3 mmol) and anhydrous sodium acetate (250 mg, 3.2 mmol) in dichloromethane (10 ml) was added dropwise a solution of alcohol (**15**) (200 mg, 0.76 mmol) in dichloromethane (40 ml) at room temperature. After 2 h further PCC (200 mg, 0.93 mmol) and sodium acetate (100 mg, 1.3 mmol) were added and the mixture was stirred for another 1 h. The solvent was evaporated and the residue was passed through a short column of silica gel (dichloromethane) to give compound (**17**) (143 mg, 73%); mp 236-237 °C (from ethanol). Anal. Calcd for $C_{13}H_6NO_3Cl$: C, 60.1; H, 2.3; N, 5.4; Cl, 13.65. Found: C, 60.3; H, 2.4; N, 5.5; Cl, 13.9; ir ν_{max} (KBr): 3600 (OH), 1660 (C=O) cm^{-1}; ^{1}H-nmr δ ($CDCl_3$): 7.39 (1 H, dd, J 8.1, 1.5, 8-H), 7.74 (1 H, dd, J 8.1, 7.6, 7-H), 7.77 (1 H, d, J 5.1, 3-H), 7.85 (1 H, dd, J 7.6, 1.5, 6-H), 8.95 (1 H, d, J 5.1, 2-H), 12.3 (1H, s, OH); ^{13}C-nmr δ ($CDCl_3$): 115.5, 120.1, 124.6, 127.6, 131.3, 133.5, 137.8, 145.9, 150.8, 153.7, 162.8, 180.5, 185.4.

5,10-Dihydro-9-hydroxybenzo[*g*]quinoline-5,10-dione (18)

A suspension of chloroquinoline (**17**) (50 mg, 0.19 mmol), KOH (32 mg, 0.57 mmol) and 10% palladium on activated carbon (10 mg) in methanol (40 ml) was hydrogenated at 2 atm for 3 h at room temperature. The mixture was then filtered through Celite and the filtrate was evaporated under reduced pressure. The residue was poured into cold water (20 ml) and the aqueous phase was neutralized by addition of diluted HCl (5%). The solution was extracted with dichloromethane (3x20 ml), and the combined organic layers were dried , filtered and concentrated. The residue was purified by column chromatography on silica gel (dichloromethane) to yield quinoline (**18**) (28 mg, 66%); mp 215-216 °C (from ethanol). Anal. Calcd for $C_{13}H_7NO_3$: C, 69.3; H, 3.1; N, 6.2. Found: C, 69.5; H, 3.0; N, 6.4; ir ν_{max} (KBr):3400br (OH), 1660 and 1630 (C=O) cm^{-1}; ^{1}H-nmr δ ($CDCl_3$): 7.38 (1 H, dd, J 8.3, 1.3, 8-H), 7.70-7.80 (2 H, m, 3-H and 7-H), 7.85 (1 H, dd, J 7.5, 1.3, 6-H), 8.63 (1 H, dd, J 7.9, 1.8, 4-H), 9.13 (1 H, dd, J 4.6, 1.8, 2-H), 12.5 (1H, s, OH); ^{13}C-nmr δ ($CDCl_3$): 116.3, 119.8, 125.2, 128.3, 130.8, 132.6, 135.5, 137.3, 148.7, 155.1, 163.1, 181.9, 186.8.

5,10-Dihydro-9-methoxybenzo[*g*]quinoline-5,10-dione (3)

To a solution of hydroxyquinone (**18**) (165 mg, 0.73 mmol) in dichloromethane (15 ml) were added Ag_2O (190 mg, 0.83 mmol) and iodomethane (0.1 ml, 1.6 mmol). After being stirred for 8 days at room temperature, the reaction mixture was filtered. The filtrate was concentrated and the residue was purified by silica gel chromatography (dichloromethane) to provide methoxyquinone (**3**) (155 mg, 84%), mp 205 °C (lit.,[3b] 198-199 °C)

Reaction of quinone (7) with 1-trimethylsilyloxy-1,3-butadiene (8)

To a stirred solution of quinone (**7**) (75 mg, 0.32 mmol) in dichloromethane (7.5 ml) was slowly added 1-trimethylsilyloxy-1,3-butadiene (**8**) (0.07 ml, 0.4 mmol) *via* a syringe, and the mixture was left at room temperature for 4 days. After evaporation of the solvent, the residue was recrystallized from cyclohexane to give adduct (**19**) (115 mg, 96%); mp 94-95 °C. Anal. Calcd for $C_{19}H_{27}NO_5Si$: C, 60.45; H, 7.2; N, 3.7. Found: C, 60.7; H, 7.3; N, 3.8; ir ν_{max} (KBr): 1760, 1700 and 1640 (C=O) cm^{-1}; ^{1}H-nmr δ ($CDCl_3$): -0.053 (9 H, s, Me_3Si), 1.22 (3 H, t, J 7.1, CH_3), 1.70-2.15 (3 H, m, 3-H and 9-H), 2.3-2.6 (2 H, m, 4-H), 2.9-3.2 (2 H, m, 2-H and 9-H), 3.16 (1 H, dd, J 6.4, 4.0, 5a-H), 3.37 (1 H, t, J 6.8, 9a-H), 4.0-4.3 (3 H, m, 2-H and OCH_2), 4.37 (1 H, t, J 4.4, 6-H), 5.7-5.9 (2 H, m, 7-H and 8-H); ^{13}C-nmr δ ($CDCl_3$): 0.06, 14.1, 20.9, 21.7, 22.1, 41.8, 44.3, 53.3, 62.8, 65.3, 126.6, 128.6, 132.5, 149.0, 154.1, 192.5, 198.2.

1-Carboethoxy-6-hydroxy-1,2,3,4,5,5a,6,9,9a,10-decahydrobenzo[*g*]quinoline-5,10-dione (20)

To a solution of adduct (**19**) (280 mg, 0.74 mmol) in THF-H_2O (9:1, 30 ml) was added dropwise 1N HCl (1.1 ml) at 0 °C and the mixture was stirred for 2 h at room temperature. The reaction mixture was partitioned between chloroform and water (1:1, 100 ml), and the organic layer was separated. The aqueous layer was extracted with chloroform (2x50 ml) and the combined organic phases were dried over $MgSO_4$ and concentrated. The residue was recrystallised from cyclohexane-benzene (1:1) to give alcohol (**20**) (130 mg, 57%); mp 149-150 °C. Anal. Calcd for $C_{16}H_{19}NO_5$: C, 62.9; H, 6.3; N, 4.6. Found: C, 63.1; H, 6.35; N, 4.7; ir ν_{max} (KBr):3440 (OH), 1720s, 1660 and 1650 (C=O) cm^{-1}; ^{1}H-nmr δ ($CDCl_3$): 1.24 (3 H, t, J 7.1, CH_3), 1.8-1.9 (2 H, m, 3-H), 2.1-2.7 (4 H, m, 4-H, 9-H and OH), 3.26 (1 H, dd, J 5.9, 4.5, 5a-H), 3.4-3.6 (2 H, m, 2-H and 9a-H), 3.78 (1 H, dt, J 13.1, 5.4, 5a-H), 4.37 (2 H, c, J 7.1, CH_2O), 5.8-6.0 (2 H, m, 7-H and 8-H); ^{13}C-nmr δ ($CDCl_3$) : 14.1, 20.6, 21.9, 22.8, 44.0, 44.3, 52.2, 63.0, 66.2, 128.0, 128.5, 132.0, 148.1, 153.8, 194.9, 198.2.

1-Carboethoxy-6-hydroxy-1,2,3,4,5,10-hexahydrobenzo[*g*]quinoline-5,10-dione (21)

To a stirred suspension of PCC (200 mg, 0.93 mmol) and anhydrous sodium acetate (100 mg, 1.3 mmol) in dichloromethane (30 ml) was added dropwise a solution of alcohol (**20**) (100 mg, 0.33 mmol) in dichloromethane (5 ml) at room temperature. After 45 min further PCC (100 mg, 0.46 mmol) and sodium acetate (50 mg, 0.63 mmol) were added and the mixture was stirred for another 30 min. The solvent was evaporated off and the residue was passed through a short column of silica gel (dichloromethane) to give compound (**21**) (84 mg, 87%); mp 141-142 °C (from cyclohexane). Anal. Calcd for $C_{16}H_{15}NO_5$: C, 63.8; H, 5.0; N, 4.65. Found: C, 63.7; H, 5.0; N, 4.65; ir ν_{max} (KBr): 3440 (OH), 1720, 1680 and 1620 (C=O) cm^{-1}; ^{1}H-nmr δ ($CDCl_3$): 1.23 (3 H, t, J 7.1, CH_3), 1.97 (2 H, dd, J 6.6, 5.3, 3-H), 2.67 (2 H, t, J 6.6, 4-H), 3.73 (2 H, t, J 5.3, 2-H), 4.20 (2 H, q, J 7.1, CH_2O), 7.21 (1 H, dd, J 6.9, 2.7, 7-H), 7.50-7.60 (2 H, m, 8-H and 9-H), 12.11 (1 H, s, OH); ^{13}C-nmr δ ($CDCl_3$): 14.0, 20.6, 21.8, 44.8, 63.1, 114.5, 119.1, 124.0, 131.2, 132.6, 135.6, 146.0, 154.6, 161.0, 179.1, 188.9.

5,10-Dihydro-6-hydroxybenzo[*g*]quinoline-5,10-dione (22)

To a stirred solution of KOH (1.0 g, 17.8 mmol) in methanol-water (1:1, 20 ml) was added a solution of carbamate (**21**) (120 mg, 0.4 mmol) in methanol (10 ml). After 15 min the solution was poured into water (20 ml) and neutralized with 5% HCl. The product was extracted with ethyl acetate (3x35 ml).and the extracts were washed with water and dried ($MgSO_4$). The solvent was removed and the residue was dissolved in benzene and DDQ (185 mg, 0.82 mmol) was then added. The stirred mixture was heated to reflux for 7 h, and after being cooled to room temperature, the reaction mixture was partitioned between dichloromethane and 5% aqueous $NaHCO_3$ (1:1, 50 ml). The organic layer was separated and the aqueous layer was extracted with dichloromethane (2x25 ml) and the combined organic phases were dried over $MgSO_4$ and concentrated. Purification of the residue by column chromatography on silica gel (CH_2Cl_2) afforded compound (**22**) (44 mg, 50%); mp 225 °C (decomp.). Anal. Calcd for $C_{13}H_7NO_3$: C, 69.3; H, 3.1; N, 6.2. Found: C, 69.5; H, 3.2; N, 6.3; ir ν_{max} (KBr): 3440 (OH), 1660 and 1620 (C=O) cm^{-1}; ^{1}H-nmr δ ($CDCl_3$): 7.37 (1 H, dd, J 8.4, 1.2, 7-H), 7.70-7.80 (2 H, m, 3-H and 8-H), 7.96 (1 H, dd, J 7.5, 1.2, 9-H), 8.67 (1 H, dd, J 8.0, 1.8, 4-H), 9.14 (1 H, dd, J 4.6, 1.8, 2-H), 12.33 (1 H, s, OH); ^{13}C-nmr δ ($CDCl_3$): 115.6, 120.6, 124.9, 127.9, 130.5, 133.2, 135.1, 137.3, 149.1, 155.5, 162.6, 180.9, 187.9.

Reaction of quinone 2 with 1-dimethylamino-1-aza-1,3-butadiene (9)

To a solution of quinone (**2**)[6] (450 mg, 2.33 mmol) in acetonitrile (50 ml) was added a solution of azadiene (**9**)[10](350 mg, 3.56 mmol) in dichloromethane (10 ml) and the mixture was left at room temperature for 1 h. Silica gel (1.5 g) was added and the mixture was stirred for 30 min and 2,3,4,6-tetrachloro-1,4-benzoquinone (*p*-chloranil) (1.80 g, 7.3 mmol) was then added and the mixture was heated to reflux for 3 h. After being cooled to room temperature, the reaction mixture was filtered through Celite. Evaporation of the solvent and purification of the residue by *column chromatography on silica (CH_2Cl_2) gave compounds* (**23**) *(68 mg, 12%) and* (**24**) (245 mg, 43%).

4-Chloro-5,10-dihydropyrido[2,3-*g*]quinoline-5,10-dione (23)

mp 220 °C (decomp.) (benzene). Anal. Calcd for $C_{12}H_5N_2O_2Cl$: C, 58.9; H, 2.1; N, 11.45; Cl, 11.5. Found: C, 58.6; H, 2.25; N, 11.2; Cl, 11.4; ir ν_{max} (KBr): 1690 (C=O) cm^{-1}; ^{1}H-nmr δ ($CDCl_3$): 7.77-7.84 (2 H, m, 3-H and 8-H), 8.71 (1 H, dd, J 8.0, 1.8, 9-H), 8.97 (1 H, d, J 5.1, 2-H), 9.19 (1 H, dd, J 4.6, 1.8, 7-H); ^{13}C-nmr δ ($CDCl_3$): 127.8, 128.3, 129.3, 131.4, 135.7, 146.4, 148.7, 150.3, 154.0, 156.0, 179.5, 180.4.

4-Chloro-5,10-dihydropyrido[3,2-*g*]quinoline-5,10-dione (24)

mp 254-255 °C (benzene). Anal. Calcd for $C_{12}H_5N_2O_2Cl$: C, 58.9; H, 2.05; N, 11.45; Cl, 11.5. Found: C, 59.0; H, 2.2; N, 11.25; Cl, 11.8; ir ν_{max} (KBr): 1690 and 1670 (C=O) cm^{-1}; ^{1}H-nmr δ ($CDCl_3$): 7.80-7.90 (2 H, m, 3-H and 7-H), 8.67 (1 H, dd, J 8.0, 1.7, 6-H), 9.00 (1 H, d, J 5.1, 2-H), 9.18 (1 H, dd, J 4.6, 1.7, 8-H); ^{13}C-nmr δ ($CDCl_3$): 126.8, 128.7, 130.9, 131.2, 135.8, 145.9, 147.6, 150.9, 154.2, 155.7, 179.2, 180.7.

Reaction of quinone (7) with 1-dimethylamino-1-aza-1,3-butadiene (9)

To a solution of quinone (**7**) (380 mg, 1.62 mmol) in dichloromethane (10 ml) was added a solution of azadiene (**9**)[12] (240 mg, 2.43 mmol) in dichloromethane (10 ml) and the mixture was left at room temperature overnight. Silica gel (1.0 g) was added and the mixture was stirred for 15 min and *p*-chloranil(1.20 g, 4.90 mmol) was then added and the mixture was heated to reflux for 3.5 h. After being cooled to room temperature, the reaction mixture was partitioned between dichloromethane and 5% aqueous $NaHCO_3$ (1:1, 100 ml). The organic layer was separated and the aqueous layer was extracted with dichloromethane (2x50 ml) and the combined organic phases were dried and concentrated. Purification of the residue by column chromatography on silica gel (CH_2Cl_2) afforded compound (**25**) (240 mg, 52%); mp 115-117 °C. Anal. Calcd. for $C_{15}H_{14}N_2O_4$: C, 62.9; H, 4.9; N, 9.8. Found: C, 63.1; H, 4.9; N, 9.6; ir ν_{max} (KBr): 1700, 1680 and 1670 (C=O) cm^{-1}; ^{1}H-nmr δ ($CDCl_3$): 1.26 (3 H, t, J 7.1, CH_3), 2.0 (2 H, m, 3-H), 2.78 (2 H, t, J 6.6, 4-H), 3.75 (2 H, t, J 5.7, 2-H); 4.18 (2 H, q, J 7.1, CH_2O), 7.66 (1 H, dd, J 7.9, 4.7, 8-H), 8.37 (1 H, dd, J 7.9, 1.7, 9-H), 9.01 (1 H, dd, J 4.7, 1.7, 7-H); ^{13}C-nmr δ ($CDCl_3$): 14.1, 21.4, 21.8, 44.8, 63.1, 127.3, 129.4, 132.8, 134.5, 144.6, 147.5, 154.3, 154.4, 178.9, 182.1.

5,10-Dihydropyrido[2,3-*g*]quinoline-5,10-dione (26)

Hydrolysis and oxidation of **25** (115 mg, 0.4 mmol) as described for **18** gave compound (**26**) (58 mg, 69%); mp 320 °C (decomp.). Anal. Calcd for $C_{12}H_6N_2O_2$: C, 68.6 H, 2.9; N, 13.3. Found: C, 68.8; H, 3.0; N, 13.6; ir ν_{max} (KBr):1670 (C=O) cm^{-1}; ^{1}H-nmr δ ($CDCl_3$): 7.87 (2 H, dd, J 8.0, 4.6, 3-H and 8-H), 8.77 (2 H, dd, J 8.0, 1.7, 4-H and 9-H), 9.18 (2 H, dd, J 4.6, 1.7, 2-H and 7-H); ^{13}C-nmr δ ($CDCl_3$): 128.4, 130.6,135.8, 148.0, 155.3, 181.0.

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