DIELS-ALDER REACTIONS OF A HYDRAZONOCROTONATE WITH BROMONAPHTHOQUINONES

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Abstract - An efficient and regiospecific synthesis of 4,6- and 4,9-disubstituted 5,10-benzo[*g*]quinolinequinone derivatives was performed through a hetero Diels-Alder reaction between methyl *(E)*-4-dimethylhydrazono-2-butenoate (**1**) and 2- or 3-bromo-5-substitued naphthoquinones (**2**) and (**3**). According to the experimental conditions used, the corresponding dihydro or aromatic compounds were isolated as the major products. The regiochemistry of the cycloadditions is governed by the position of the bromine atom at C-2 or C-3 of the quinone.

Polycyclic aromatic alkaloids such as sampangine[1] and eupomatidines[2] possess the naphthonaphthyridin-7-one skeleton (**I**). Furthermore, several A- and B-ring substituted sampangines were described for antifungal and antimycobacterial activities.[3] Their synthesis involves in the key step a hetero Diels-Alder reaction between crotonaldehyde *N*,*N*-dimethylhydrazone or its 4-methoxyl derivative and 2-bromonaphthoquinone.[3,4] On the other hand, several pyridazinones were known for their pharmacological properties.[5] Among them, antimitotic[5a] and cardiotonic[5d] activities seem attractive. In order to obtain D-ring functionalized pyridazinoneazaanthrones (**II**) for a structure-activity relationship study on antifungal or antitumor properties, we plan to investigate the reactivity of methyl *(E)*-4-dimethylhydrazono-2-butenoate (**1**)[6] towards naphthoquinones (Scheme 1).

The usefulness of α,β-unsaturated *N*,*N*-dimethylhydrazones has been well exploited in hetero Diels-Alder reactions towards quinones.[7-9] A substitution at C-3 by an electron releasing goup facilitated the

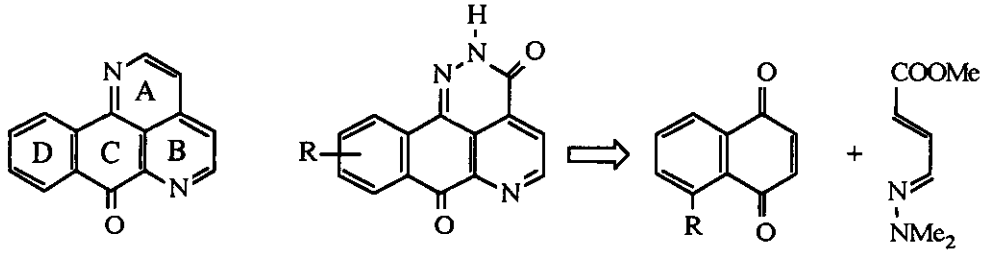
cycloadditions.[7b] In contrast, azadiene (**1**) has not yet been employed in [4+2] cycloadditions. In our first synthetic approach to pyridazinoneazaanthrones (**II**), we observed that **1** reacts slowly with 1,4-naphthoquinone (**III**) or juglone (**IV**) at reflux of toluene and the 1,4-dihydro-5,10-benzo[*g*]quinolinequinone derivatives were obtained in low yields (16 % and 9 % respectively). Furthermore, starting from **IV** no regioselectivity was observed.[10] The less reactivity of azadiene (**1**) towards these quinones could be explained by the presence at C-4 of the electron withdrawing methoxycarbonyl group. Then, we turned our attention to the use of 2- or 3-bromonaphthoquinones (**2**) or (**3**) since this kind of halogenated dienophiles were known to be more reactive and to afford regiospecific cycloadditions with electron rich azadienes.[11,12]

We describe in this paper an efficient and regiospecific synthesis of 4,6- and 4,9-disubstituted 5,10-benzo[*g*]quinolinequinones through the hetero Diels-Alder reaction of **1** and **2** or **3**. According to the experimental conditions used, the corresponding dihydro or aromatic compounds were isolated as the major products. The results are summerized in Scheme 2 and Table 1.

In method A, a toluene solution of azadiene (**1**) and the corresponding quinone was heated under reflux for a variable time. The tetrahydro adducts were not observed. But, a complex mixture was formed from which the dihydro *N,N*-dimethylamino (**4**) or (**5**), the dihydro N-H derivatives (**6**) or (**7**) and some aromatized products (**8**) or (**9**) are isolated. The presence of **6** or **7** is probably due to the N-N bond cleavage from the unstable dihydro derivatives (**4**) or (**5**) by hydrogen bromide liberated from the primary adducts. Indeed, the use of an equivalent of sodium bicarbonate (method B) permits to avoid or to diminish their formation. Carrying out the Diels-Alder reactions in the presence of two equivalents of sodium bicarbonate at reflux of xylene (method C) gave directly the aromatized compounds (**8**) or (**9**) in good yields.

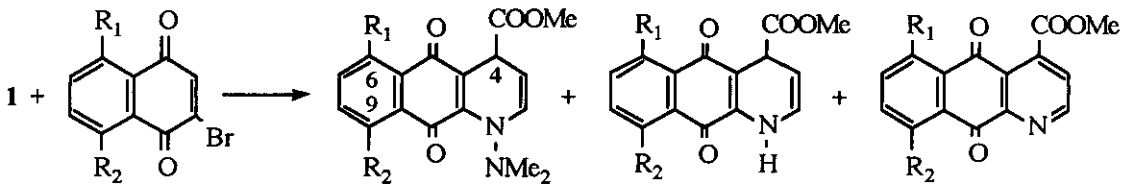
Starting from 2-bromonaphthoquinones (**2a**) or (**2b**) and azadiene (**1**) and following method C, dimethylaminonaphthoquinones (**10a**) or (**10b**) were isolated in 11 and 15 % yields respectively as well as the aromatized products (**8a**) or (**8b**). Formation of **10a** or **10b** resulted from a nucleophilic addition of the liberated dimethylamine on the starting quinone followed by hydrogen bromide elimination. With 3-bromomethyljuglone (**3c**), this side reaction was only observed in the conditions used for methods A and B. Thus, in method A, dimethylaminomethyljuglones (**10c**) and (**11c**) were isolated in 12 % yield (ratio **10c** / **11c** : 1 / 1) as well as compounds (**5c**), (**7c**) and (**9c**) while using sodium bicarbonate (method B), a single regioisomer (**11c**) was obtained in the same yield. These aminoquinones are identified by comparison of their physical and spectral data with those of authentic samples prepared through a direct

addition of dimethylamine upon **2** or **3**.[13] However, in the presence of sodium bicarbonate, an opposite regiochemistry was observed comparatively to that given in its absence.

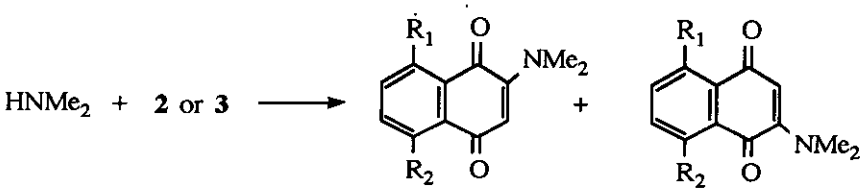


I **II** **III** : R = H **IV** : R = OH **1**

Scheme 1



2 or **3** **4** or **5** **6** or **7** **8** or **9**



10 **11**

	R_1	R_2	Regioisomer
2a	H	H	
2b	OH	H	2-bromo
2c	OMe	H	2-bromo
3b	H	OH	3-bromo
3c	H	OMe	3-bromo
10a	H	H	
10b	H	OH	2-dimethylamino
10c	H	OMe	2-dimethylamino
11c	H	OMe	3-dimethylamino

	R_1	R_2	Regioisomer
4a, 6a, 8a	H	H	
4b, 6b, 8b	OH	H	4,6-
4c, 6c, 8c	OMe	H	4,6-
5b, 7b, 9b	H	OH	4,9-
5c, 7c, 9c	H	OMe	4,9-

Scheme 2

Table 1. Diels-Alder reaction of azadiene (**1**) towards bromonaphthoquinones (**2**) and (**3**).

Bromo-quinone	R_1	R_2	Method	Reaction time (h)[a]	Compounds	Ratio[d]	Overall yield % [d]
2a	H	H	A	5	**6a + 8a**	71 / 29	41
			C	24	**8a**[e]		53
2b	OH	H	A	4	**4b + 6b + 8b**	52 / 33 / 15	39
			B	4	**4b + 8b**	91 / 9	44
			C	5	**8b**[e]		40
2c	OMe	H	A	19	**6c + 8c**	43 / 57	46
			B	19	**6c + 8c**	8 / 92	76
			B	5	**4c + 8c**	85 / 15	48
			C	19	**8c**		45
3b	H	OH	A	4	**7b + 9b**	52 / 48	52
			B	4[b]	**7b + 9b**	5 / 95	74
			B	2[c]	**5b + 7b**	91 / 9	55
			C	4	**9b**		68
3c	H	OMe	A	19	**5c + 7c + 9c**[e]	38 / 24 / 38	45
			B	19	**5c + 7c + 9c**[e]	75 / 10 / 15	73
			B	5	**5c + 7c + 9c**[e]	81 / 16 / 3	37
			C	19	**9c**		48

[a]The evolution of the reaction is followed by tlc.

[b]A column chromatography on an acidic silica gel gives **9b** as the major product.

[c]A column chromatography on a neutral silica gel permits to isolate the dihydro *N*,*N*-dimethylamino derivative (**5b**) as the major product.

[d]Evaluated from the pure isolated products.

[e]Aminoquinones (**10**) or (**11**) are also formed.

Concerning the regiochemistry of the cycloadditions, the 4,6- regioisomers (**4**), (**6**) and (**8**) were obtained from 2-bromonaphthoquinones while starting from the 3-bromo dienophiles, the 4,9-derivatives (**5**), (**7**) or (**9**) were formed. Structural assignment was made on the basis of their ^{1}H-nmr spectral data. Indeed, the

nitrogen atom exerts a significant long range effect on the chemical shifts of the peri-hydroxyl group in the corresponding regioisomers. Thus, the 6-OH appears deshielded in the dihydro derivatives (**4b**) and (**6b**) and shielded in the aromatic **8b** while the contrary is observed with the 9-OH in **5b**, **7b** and **9b** respectively. These values, given in Table 2, are in good agreement with those previously reported for analogous dihydro[9a] and aromatic[12] compounds. To assign the structure of the methoxylated derivatives, **8b** and **9b** were separately treated with methyl iodide and silver oxide.[14] The obtained compounds were identical with **8c** and **9c** respectively. This chemical transformation demonstrates that the regiospecificity observed is independant on the nature of the 5-substituent (OH or OMe) on the bromonaphthoquinone and indicates that the nucleophilic end of this 1-azadiene bearing an electron withdrawing group adds also exclusively at the unsubstituted carbon of the dienophile (**2**) or (**3**).

Table 2. ^{1}H-Nmr spectral data of the regioisomeric benzo[*g*]quinolinequinones (300 MHz, $CDCl_3$, δ ppm)

	OH	NH	H-2	H-3	H-4	OMe	COOMe	NMe_2
4b	12.22		6.42	5.30	4.54		3.74	2.72
5b	11.74		6.42	5.31	4.54		3.72	2.73
4c			6.39	5.22	4.54	3.96	3.71	2.71
5c			6.41	5.24	4.54	3.98	3.71	2.72
6b	12.51	7.15	6.31	5.12	4.57		3.75	
7b	11.41	7.05	6.31	5.12	4.57		3.73	
6c		6.78	6.29	5.03	4.58	3.98	3.72	
7c		7.07	6.32	5.18	4.59	4.02	3.72	
8b	11.98		9.20	7.65			4.10	
9b	12.37		9.16	7.62			4.06	
8c			9.10	7.59		4.08	4.05	
9c			9.15	7.57		4.08	4.07	

EXPERIMENTAL

Melting points were taken in a capillary tube using a Büchi 510 apparatus and are corrected. Ir spectra were performed on a Perkin-Elmer 1310 spectrophotometer. The ^{1}H-nmr spectra were recorded at 300 MHz on a

Bruker AM 300 spectrometer. Mass spectra were performed by direct ionisation (EI at 70 eV) on an AEI MS 902 apparatus. Elemental analysis were made at the Centre de Microanalyse du CNRS at Solaize. Column chromatography was carried out with Matrex (60 Å, 35-70 μm) acidic silca gel or Merck (60 Å, 40-63 μm, pH 7.0±0.5). Bromonaphthoquinone (**2a**) and 2-bromo-5-hydroxynaphthoquinone (**2b**) were prepared according to Grunwell *et al.*[15] 3-Bromo-5-hydroxynaphthoquinone (**3b**) was obtained by treating juglone with bromine in glacial acetic acid.[16] By this method 13 % of the 2-bromo derivative (**2b**) was also formed which was eliminated by recrystallization from acetone. Methylation of **2b** and **3b** gave respectively **2c** and **3c**.[17] The preparation of *N*,*N*-dimethylhydrazonoglyoxal was performed according to a known procedure.[18]

Synthesis of methyl *(E)*-4-dimethylhydrazono-2-butenoate (1)[6]

This azadiene was prepared by a modified Wittig procedure to that described by Severin *et al.*[18] A 60 % mineral suspension of sodium hydride (0.4 g, 10 mmol) was washed with hexane, suspended in anhydrous THF (20 ml) and introduced in a round bottom flask. Methyl trimethylphosphonoacetate (1.8 g, 10 mmol) was added *via* a syringe under stirring. The reaction mixture was heated at 30-35 °C for 30 min. Then, *N*,*N*-dimethylhydrazonoglyoxal (1 g, 10 mmol) was slowly added. Stirring and heating at 40 °C were maintained for 2 h. After the usual work-up and distillation under reduced pressure, azadiene (**1**) was isolated as a liquid which solidify after storage in the refrigerator. Yield : 1.025 g (66 %); bp 80 °C (0.2 mm Hg).

Cycloadditions of azadiene (1) to bromoquinones (2) or (3). General procedure

Method A: Azadiene (**1**) (0.234 g, 1.5 mmol) was added under nitrogen to a solution of the corresponding bromoquinone (**2**) or (**3**) (1 mmol) in freshly distilled toluene (15 ml). Then, the reaction mixture was stirred and heated at 110 °C for a variable time, the evolution of the reaction being followed by tlc. After filtration and evaporation of the solvent, compounds (**4**) or (**5**), (**6**) or (**7**) and (**8**) or (**9**) are isolated by column chromatography on acidic or neutral silica gel using as eluent AcOEt / hexane (1 / 1) for the hydroxylated derivatives or (4 / 1) for the methoxylated ones.

Method B: In this method, $NaHCO_3$ (0.084 g, 1 mmol) was added to the same solution as above (method A) before heating the reaction mixture.

Method C: Azadiene (**1**) (0.234 g, 1.5 mmol) was added under nitrogen to a solution of the corresponding bromoquinone(1 mmol) in freshly distilled xylene (20 ml). Then, $NaHCO_3$ (0.168 g, 2 mmol) was added and the reaction mixture was stirred and heated at 140 °C for a variable time, the evolution of the reaction being followed by tlc. After filtration and evaporation of the solvent, the aromatized compounds (**8**) or (**9**) are isolated by column chromatography on silica gel and recrystallized from ethanol.

1-*N*,*N*-Dimethylamino-6-hydroxy-4-methoxycarbonyl-1,4-dihydro-5,10-benzo[*g*]quinolinequinone (4b)

Dark brown needles, mp 195 °C (ethanol). Ir (KBr): 1730, 1680, 1655 cm^{-1}. ^{1}H-Nmr ($CDCl_3$, 300 MHz): δ 12.22 (1H, s, OH); 7.52 (1H, H-7 or H-9, d, J = 4.5 Hz); 7.51 (1H, H-7 or H-9, d, J = 4.8 Hz); 7.19 (1H, H-8, dd, J = 4.5 and 4.8 Hz); 6.42 (1H, H-2, dd, J = 8.0 and 0.5 Hz); 5.30 (1H, H-3, dd, J = 8.0 and 4.8 Hz); 4.54 (1H, H-4, dd, J = 4.8 and 0.5 Hz); 3.74 (3H, s, $COOCH_3$); 2.72 (6H, s, $N(CH_3)_2$). Anal. Calcd for $C_{17}H_{16}N_2O_5$: C, 62.19; H, 4.91; N, 8.53. Found: C, 62.15; H, 4.94; N, 8.32.

1-*N*,*N*-Dimethylamino-6-methoxy-4-methoxycarbonyl-1,4-dihydro-5,10-benzo[*g*]quinolinequinone (4c)

Red powder, mp 214 °C (ethanol). Ir (KBr): 1735, 1680, 1645, 1635 cm^{-1}. ^{1}H-Nmr ($CDCl_3$, 300 MHz): δ 7.65 (1H, H-9, dd, J = 7.6 and 1.3 Hz); 7.59 (1H, H-8, dd, J = 7.7 and 8.0 Hz); 7.22 (1H, H-7, dd, partially masqued by $CDCl_3$); 6.39 (1H, H-2, d, J = 7.9 Hz); 5.22 (1H, H-3, dd, J = 7.9 and 4.9 Hz); 4.54 (1H, H-4, d, J = 4.9 Hz); 3.96 (3H, s, OCH_3); 3.71 (3H, s, $COOCH_3$); 2.71 (6 H, s, $N(CH_3)_2$); ms (m/z): 342 (3) (M^+), 297 (16), 283 (40), 265 (41), 240 (100). Hrms calcd for $C_{18}H_{18}N_2O_5$: 342.1216. Found: 342.1215. A partial aromatization of this compound occurs by recrystallization. For this reason microanalysis data are not satisfactory.

1-*N*,*N*-Dimethylamino-9-hydroxy-4-methoxycarbonyl-1,4-dihydro-5,10-benzo[*g*]quinolinequinone (5b)

mp 210 °C (ethanol). Ir (KBr): 1740, 1640, cm^{-1}. ^{1}H-Nmr ($CDCl_3$, 300 MHz): δ 11.74 (1H, s, OH); 7.56 (1H, H-6 or H-8, d, J = 3.2 Hz); 7.55 (1H, H-6 or H-8, d, J = 6.4 Hz); 7.18 (1H, H-7, dd, J = 6.4 and

3.2 Hz); 6.42 (1H, H-2, d, J = 7.8 Hz); 5.31 (1H, H-3, dd, J = 7.8 and 5.2 Hz); 4.54 (1H, H-4, d, J = 5.2 Hz); 3.72 (3H, s, $COOCH_3$); 2.73 (6 H, s, $N(CH_3)_2$). Due to the very fast aromatization of this compound, microanalysis data are not satisfactory.

1-*N*,*N*-Dimethylamino-9-methoxy-4-methoxycarbonyl-1,4-dihydro-5,10-benzo[*g*]quinolinequinone (5c)

Red crystals, mp 134 °C (ethanol). Ir (KBr): 1730, 1680, 1660, 1635 cm^{-1}. ^{1}H-Nmr ($CDCl_3$, 300 MHz): δ 7.67 (1H, H-6, dd, J = 7.7 and 1.2 Hz); 7.58 (1H, H-7, dd, J = 7.7 and 8.3 Hz); 7.20 (1H, H-8, dd, J = 8.3 and 1.1 Hz); 6.41 (1H, H-2, dd, J = 8.0 and 0.5 Hz); 5.24 (1H, H-3, dd, J = 8.0 and 4.7 Hz); 4.54 (1H, H-4, dd, J = 4.7 and 0.5 Hz); 3.98 (3H, s, OCH_3); 3.71 (3H, s, $COOCH_3$); 2.72 (6 H, s, $N(CH_3)_2$). Due to the very fast aromatization of this compound, microanalysis data are not satisfactory.

4-Methoxycarbonyl-1,4-dihydro-5,10-benzo[*g*]quinolinequinone (6a)

Black crystals, mp 186 °C (ethanol). Ir (KBr): 1735, 1680, 1655 cm^{-1}. ^{1}H-Nmr ($CDCl_3$, 300 MHz): δ 8.09 (1H, H-6 or H-9, dd, J = 7.6 and 1.3 Hz); 8.06 (1H, H-6 or H-9, dd, J = 7.6 and 1.4 Hz); 7.74 (1H, H-7 or H-8, dt, J = 7.6 and 1.4 Hz); 7.65 (1H, H-7 or H-8, dt, J = 7.6 and 1.4 Hz); 6.97 (1H, br s, NH); 6.32 (1H, m, H-2); 5.10 (1H, m, H-3); 4.62 (1H, H-4, d, J = 4.5 and 1.0 Hz); 3.74 (3H, s, $COOCH_3$). Anal. Calcd for $C_{15}H_{11}NO_4$: C, 66.91; H, 4.11; N, 5.20. Found: C, 66.98; H, 4.09; N, 5.29.

6-Hydroxy-4-methoxycarbonyl-1,4-dihydro-5,10-benzo[*g*]quinolinequinone (6b)

This compound was obtained as a mixture with **4b** from which it was not separated. Ir (KBr): 3360, 1730, 1680, 1650 cm^{-1}. ^{1}H-Nmr ($CDCl_3$, 300 MHz): δ 12.51 (1H, s, OH); 7.60 (1H, H-9, d, J = 7.4 Hz); 7.51 (1H, H-8, dd J = 7.8 and 7.4 Hz); 7.26 (1H, H-7, partially masqued by $CDCl_3$); 7.15 (1H, br s, NH); 6.31 (1H, m, H-2); 5.12 (1H, m, H-3); 4.57 (1H, H-4, d, J = 4.7 Hz); 3.75 (3H, s, $COOCH_3$).

6-Methoxy-4-methoxycarbonyl-1,4-dihydro-5,10-benzo[*g*]quinolinequinone (6c)

Dark red powder, mp 204 °C (ethanol). Ir (KBr): 1740, 1680, 1660, 1635 cm^{-1}. ^{1}H-Nmr ($CDCl_3$, 300 MHz): δ 7.75 (1H, H-9, dd, J = 7.7 and 1.0 Hz); 7.60 (1H, H-8, dd J = 7.7 and 7.4 Hz); 7.32 (1H, H-7,

dd, J = 7.7 and 1.0); 6.78 (1H, br s, NH); 6.29 (1H, m, H-2); 5.03 (1H, m, H-3); 4.58 (1H, H-4, dd, J = 4.4 and 1.0 Hz); 3.98 (3H, s, OCH_3); 3.72 (3H, s, $COOCH_3$); ms (m/z): 299 (6) (M^+), 297 (17), 265 (34), 240 (100). Hrms Calcd for $C_{16}H_{13}NO_5$: 299.0794. Found: 299.0793. A partial aromatization of this compound occurs by recrystallization. For this reason microanalysis data are not satisfactory.

9-Hydroxy-4-methoxycarbonyl-1,4-dihydro-5,10-benzo[*g*]quinolinequinone (7b)

Black crystals, mp 177 °C (ethanol). Ir (KBr): 3360, 1750, 1670, 1625 cm^{-1}. ^{1}H-Nmr ($CDCl_3$, 300 MHz): δ 11.41 (1H, s, OH); 7.61 (2H, m, aromat.); 7.16 (1H, m, aromat.); 7.05 (1H, br s, NH); 6.31 (1H, m, H-2); 5.12 (1H, m, H-3); 4.57 (1H, H-4, d, J = 5.0 Hz); 3.73 (3H, s, $COOCH_3$). Anal. Calcd for $C_{15}H_{11}NO_5$, 0.2 H_2O: C, 62.37; H, 3.97; N, 4.84. Found: C, 62.59; H, 4.12; N, 4.85.

9-Methoxy-4-methoxycarbonyl-1,4-dihydro-5,10-benzo[*g*]quinolinequinone (7c)

Dark red powder, mp 83 °C (ethanol). Ir (KBr): 1740, 1680, 1660, cm^{-1}. ^{1}H-Nmr ($CDCl_3$, 300 MHz): δ 7.78 (1H, H-6, dd, J = 7.7 and 1.0 Hz); 7.68 (1H, H-7, dd, J = 8.5 and 7.7 Hz); 7.25 (1H, H-8, dd, J = 8.5 and 1.0); 7.07 (1H, br s, NH); 6.32 (1H, m, H-2); 5.18 (1H, m, H-3); 4.59 (1H, H-4, dd, J = 5.0 and 1.0 Hz); 4.02 (3H, s, OCH_3); 3.73 (3H, s, $COOCH_3$). Anal. Calcd for $C_{16}H_{13}NO_5$:, 0.5 H_2O: C, 62.33; H, 4.50; N, 4.54. Found: C, 62.09; H, 4.25; N, 4.63.

4-Methoxycarbonyl-5,10-benzo[*g*]quinolinequinone (8a)

Yellow powder, mp 190 °C (ethanol). Ir (KBr): 1740, 1685, 1670 cm^{-1}. ^{1}H-Nmr ($CDCl_3$, 300 MHz): δ 9.17 (1H, H-2, d, J = 4.6 Hz); 8.42 (1H, m, H-6 or H-9); 8.28 (1H, m, H-6 or H-9); 7.78 (2H, m, H-7 and H-8); 7.63 (1H, H-3, d, J = 4.6 Hz); 4.08 (3H, s, $COOCH_3$). Anal. Calcd for $C_{15}H_9NO_4$: C, 67.42; H, 3.39; N, 5.24. Found: C, 67.55; H, 3.28; N, 5.20.

6-Hydroxy-4-methoxycarbonyl-5,10-benzo[*g*]quinolinequinone (8b)

Orange powder, mp 275 °C (ethanol). Ir (KBr): 1730, 1670, 1630 cm^{-1}. ^{1}H-Nmr ($CDCl_3$, 300 MHz): δ 11.98 (1H, s, OH); 9.20 (1H, H-2, d, J = 4.6 Hz); 7.97 (1H, H-9, d, J = 7.3 Hz); 7.78 (1H, H-8, dd, J= 8.4 and 7.3 Hz); 7.65 (1H, H-3, d, J = 4.6 Hz); 7.39 (1H, H-7, d, J = 8.4 Hz); 4.10 ((3H, s, $COOCH_3$).

Anal. Calcd for $C_{15}H_9NO_5$: C, 63.60; H, 3.20; N, 4.94. Found: C, 63.61; H, 3.38; N, 4.84.

6-Methoxy-4-methoxycarbonyl-5,10-benzo[*g*]quinolinequinone (8c)

Dark brown powder, mp 219 °C (ethanol). Ir (KBr): 1715, 1680, 1665 cm^{-1}. ^{1}H-Nmr ($CDCl_3$, 300 MHz): δ 9.10 (1H, H-2, d, J = 4.7 Hz); 8.06 (1H, H-9, d, J = 7.7 Hz); 7.80 (1H, H-8, dd, J = 8.1 and 7.7 Hz); 7.59 (1H, H-3, d, J = 4.7 Hz); 7.40 (1H, H-7, d, J = 8.1 Hz); 4.08 ((3H, s, OCH_3); 4.05 ((3H, s, $COOCH_3$). Anal. Calcd for $C_{16}H_{11}NO_5$, 0.16 H_2O: C, 64.00; H, 3.80; N, 4.66. Found: C, 64.16; H, 3.71; N, 4.67.

***9-Hydroxy-4-methoxycarbonyl-5,10-benzo[g]quinolinequinone* (9b)**

Brown powder, mp 258 °C (ethanol). Ir (KBr): 1730, 1670, 1630 cm^{-1}. ^{1}H-Nmr ($CDCl_3$, 300 MHz): δ 12.37 (1H, s, OH); 9.16 (1H, H-2, d, J = 4.7 Hz); 7.79 (1H, H-6, d, J = 8.3 Hz); 7.73 (1H, H-7, dd, J = 8.2 and 8.3 Hz); 7.62 (1H, H-3, d, J = 4.7 Hz); 7.38 (1H, H-8, d, J = 8.2 Hz); 4.06 ((3H, s, $COOCH_3$). Anal. Calcd for $C_{15}H_9NO_5$, 0.33 H_2O: C, 62.31; H, 3.36; N, 4.84. Found: C, 62.28; H, 3.33; N, 4.76.

9-Methoxy-4-methoxycarbonyl-5,10-benzo[*g*]quinolinequinone (9c)

Dark brown powder, mp 132 °C (ethanol). Ir (KBr): 1730, 1690, 1670 cm^{-1}. ^{1}H-Nmr ($CDCl_3$, 300 MHz): δ 9.15 (1H, H-2, d, J = 4.7 Hz); 7.91 (1H, H-6, dd, J = 7.7 and 1.0 Hz); 7.78 (1H, H-7, dd J = 8.4 and 7.7 Hz); 7.57 (1H, H-3, d, J = 4.7 Hz); 7.41 (1H, H-8, dd, J = 8.4 and 1.0 Hz); 4.08 ((3H, s, OCH_3); 4.07 ((3H, s, $COOCH_3$). Anal. Calcd for $C_{16}H_{11}NO_5$:, 0.16 H_2O: C, 64.00; H, 3.80; N, 4.66. Found: C, 64.05; H, 3.79; N, 4.68.

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10. A toluene solution (10 ml) of **IV** (0.111 g, 0.638 mmol) and **1** (0.150 g, 0.961 mmol) was heated under reflux for 5 hours. After the usual work-up, the 1,4-dihydro-5,10-benzo[*g*]quinolinequinones (**6**) and (**7**) were obtained in 9 % overall yield. The ratio **6** / **7** : 1 / 1 was determined from the ^{1}H-Nmr spectrum of the mixture (300 MHz, $CDCl_3$); L. Chaker, F. Pautet, and H. Fillion, *unpublished results*.

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