THE REGIOCHEMISTRY OF 6- AND 7-CHLORO-5,8-QUINOLINEQUINONES

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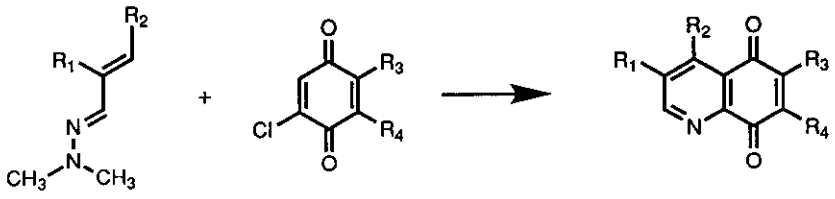
Abstract - The cycloaddition of 1-aza-1,3-dienes to benzoquinones, specifically halogenated benzoquinones, has been carried out successfully. The comparison of products so obtained with substances of known structure confirms the orientation of the process as previously postulated. It has also been shown that the regiochemistry of the reactions is determined by the sole position of the halogen and is independent of any other electronic effect. Other regiospecific transformations have been observed using the chloroquinolinequinones now made readily available. Finally, useful correlations of structures to nmr spectra have also been drawn.

1-Aza-1,3-dienes have recently been proposed as effective partners in [4 + 2] cycloadditions[1] and in particular for the preparation of azaanthracene derivatives.[1-3] The presence of an electron-donating group in the 1-position facilitates the "normal" process[1] while 1-acyl or sulfonyl[4] and 2-cyano[5] substituents promote the reaction with electron-rich philodienes. Subsequently, 1-dimethylamino-1-aza-1,3-dienes have been shown to combine regioselectively with some naphthoquinones in a plausible manner.[2,3] However the effect of the azomethine group remains unclear and the overall orientation of the cycloaddition though probable relies on the identification of isomers that could be thermally equilibrated products.[1] The situation is markedly different from that of 1,3-dioxy-2-aza-1,3-dienes in which all the electronic effects are complementary.[6]

For eventual applications in synthesis, unambiguous proof of structure can most readily be acquired by direct comparison of aromatized cycloaddition products with compounds of well established identity. In this context, such candidates are limited to bicyclic substances such as 6- and 7-chloro-[7,8] or -methoxy-5,8-quinolinequinones.[9] However previous attempts[10] to carry out comparable reactions are either unpublished[1b] or provided only benzofuran derivatives,[11] a common result of the greater ease of monocyclic quinones to aromatize.

Initial experiments involving 1-dimethylamino-3-methyl-1-azabuta-1,3-diene (**1a**) and either 2,5- or 2,6-dichlorobenzoquinones (**2a, b**), under a variety of conditions (temperature, solvent, etc.), produced as the sole identifiable products tricyclic substances (12 and 22% respectively), probably the corresponding 1,5- and 1,8-diazaanthraquinones resulting from double additions of the diene to the quinones. The isomeric chloroquinolinequinones required for eventual proof of structure or for the preparation of unsymmetrically substituted diazaanthraquinones were later obtained by operating at room temperature with dilute solutions of an excess of the benzoquinone (2 equivalents) in the presence of a small amount of acetic acid (1 equivalent). Replacement of the dimethylamino substituent on the diene by a less effective electron-donating group in the hope of obtaining a more selective reaction in fact inhibited the process completely. Ultimately, addition of the original azadiene to a boiling solution of the substrate (**2a, b**) in dichloroethane or toluene provided the best results (i.e. 71 and 56%) which were not significantly altered by resorting to brominated quinones.

Similar reactions with 2-chloro-5- or 6-methoxybenzoquinones (**2c, d**) presented no particular problem and proceeded efficiently at room temperature (73% in both cases) (**3c, d**). These model compounds were however of limited usefulness since among other considerations stated above only a 6-methoxy-5,8-quinolinequinone[9] had previously been described. In turning to isomeric alkylchloroquinolinequinones, the application of 1-azapentadiene (**1b**) was hampered by significantly greater steric hindrance and the non complementarity of the electronic effects involved. Hence yields of reactions with chloromethoxybenzo-quinones (**2c, d**) fell off sharply and even less could be obtained from dichlorobenzoquinones (Scheme I).



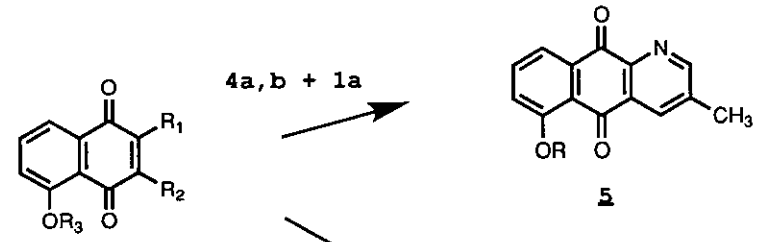
1 **2** **3**

	R_1	R_2
a	CH_3	H
b	H	CH_3
c	H	H

	R_3	R_4
a	Cl	H
b	H	Cl
c	OCH_3	H
d	H	OCH_3

	R_1	R_2	R_3	R_4
a	CH_3	H	Cl	H
b	CH_3	H	H	Cl
c	CH_3	H	OCH_3	H
d	CH_3	H	H	OCH_3
e	H	CH_3	OCH_3	H
f	H	CH_3	H	OCH_3
g	H	H	Cl	H
h	H	H	H	Cl
i	H	H	OCH_3	H
j	H	H	H	OCH_3

Scheme I



4 **5** **6**

	R_1	R_2	R_3
a	Cl	H	H
b	Cl	H	CH_3
c	H	Cl	H
d	H	Cl	CH_3

a R=H
b R=CH_3

Scheme II

Access to chloro-5,8-quinolinequinones[7,8] (**3g, h**) of established structure by the cycloaddition route required the use of an otherwise unsubstituted 1-dimethylamino-1-azabutadiene (**1c**). Some corresponding electron-rich butadienes show poor reactivity towards benzoquinones,[12] a probable consequence of low electron density at the terminal C-4 position. This behavior was also observed in the present circumstance and though no more than 26 and 36% of the desired chloroquinolinequinones (**3g, h**) could be obtained, the preparations are extremely simple. Moreover, direct comparison of these substances with authentic materials finally confirmed the predicted orientation conclusively.

With a number of quinolinequinones at hand, correlations of spectral data to the structure of isomeric substances became gratifyingly apparent. In the nmr spectra, small but consistent downfield shifts of ~ 0.1 ppm are observed for the 4-H signal of 6-chloro derivatives (**3a, g**) with respect to the 7-substituted isomers (**3b, h**). A similar shift, due to the proximity of the nitrogen atom, is shown in the case of the 7-H signal, as compared to that of 6-H, in all 6- and 7-methoxyquinolinequinones (**3c-f, i, j**).

Hydroxyl and methoxyl or acetoxyl groups in the 5-position of naphthoquinones are well known to produce definite but opposite effects in cycloadditions with more or less polar dienes.[13] Such reactions with 1-aza-1,3-dienes have previously been carried out and the resulting structures identified by the usual criteria now found to be valid. However with polar homodienes such processes are not always completely regioselective[14] and a sharper and more flexible level of discrimination (i.e. regiospecificity) is introduced by placing a halogen atom at either of the strategic 2- or 3-positions which either strengthens or submerges existing constraints.[15] This modulation of electronic effects has not previously been tested in the case of azadienes but the reaction of 1-azabuta-1,3-dienes (**1a**) with 2- and 3-chlorojuglones (**4a, c**) was found to provide exclusive formation of regioisomers (**5a**) and (**6a**) respectively. The corresponding juglone methyl ethers (**4b, d**) with inversed electronic effects nevertheless gave similar results (**5b** and **6b**). Once again structures analogous to those derived unambiguously are corroborated by spectral data. Nmr spectra of benzo[*g*]quinolinequinones (**5,6**) show that the nitrogen atom exerts a significant long range effect and deshields the 9- proton with respect to

the comparable one in position 6 (Scheme II).

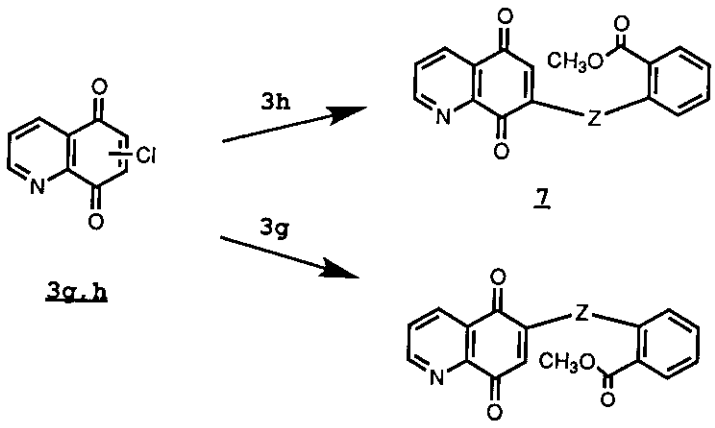
The regioselectivity of reactions requiring 6- and 7-chloro-5,8-quinodinequinones has been evaluated on occasion[16] but the number of potentially interesting cases has been restricted in comparison to other quinonic systems by the limited accessibility of appropriate substrates. Henceforth readily available, these quinolinequinones have now been submitted to recently developed methods of regiospecific substitution by salicylate[17] and *N*-mesylanthranilate[18] and afforded isomeric intermediates for the preparation of bikaverin isosteres (Scheme III). In other approaches involving cycloadditions of electron-rich dienes where nucleophilic attack occurs at the position adjacent to that of the halogen,[15] completely regiospecific processes have been obtained in high yield (Scheme IV). As in preceding instances, all structures are confirmed by significant nmr shifts.

EXPERIMENTAL

All melting points were taken for samples in capillary tubes with a Thomas-Hoover apparatus and are not corrected. The ir spectra were determined on a Perkin Elmer Model 1600 FT-IR spectrophotometer and nmr spectra were recorded with a Varian XL-200 or Bruker AC300 spectrometer using tetramethylsilane as an internal standard. Mass spectra were obtained with a Hewlett-Packard 5995A spectrometer. ICN SiliTech 32-63 60A for flash chromatography was used throughout in a product-to-adsorbent ratio of 1:50-100. Elemental analyses were carried out by Galbraith Laboratories, Inc., Knoxville, TN. Exact masses were provided by the Laboratoire de spectrométrie de masse, Université de Montréal, Qué.

I Cycloaddition of 1-azadienes to quinones.

Procedure A: To a solution of the halogenated quinone (**2a-d**) (1.00 mmol) in CH_3CN or CH_2Cl_2 (15 ml) was added the azadiene[19] (**1a-c**) (1.10 mmol) in the same solvent (5 ml). The mixture was stirred (6 h - 5 d) then evaporated to dryness. Flash chromatography of the crude product on silica gel using the mixture CH_2Cl_2 - AcOEt (10:1 to 5:1) as eluant afforded the desired quinolinequinone (**3a-j**).



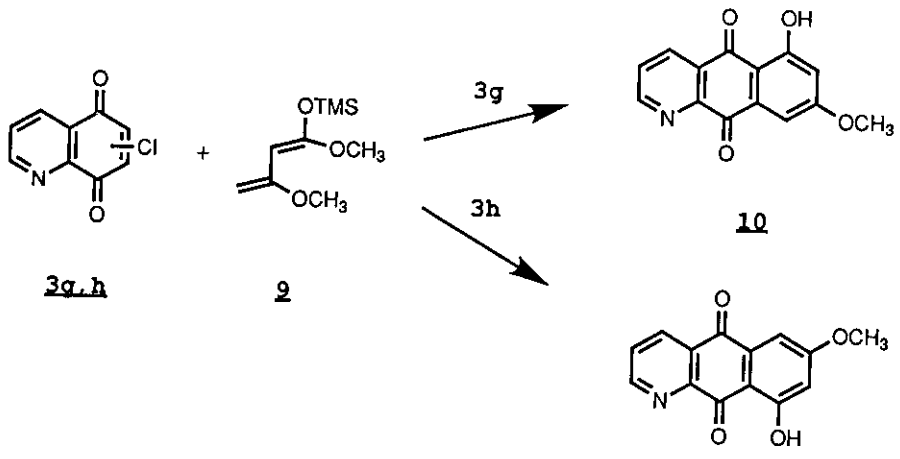
3g,h

7

8

a Z=O
b Z=NSO_2CH_3

Scheme III



3g,h

9

10

11

Scheme IV

Procedure B: To a solution of the halogenated quinone (2.00 mmol) in CH_2Cl-CH_2Cl (200 ml) at reflux temperature was added the azadiene (1.00 mmol) in the same solvent (5 ml). The mixture was maintained at the same temperature for 1.5 h then cooled and evaporated. Purification of the product was carried out as in procedure A.

Procedure C: A mixture of the halogenated quinone (2.00 mmol), the azadiene (1.00 mmol), CH_3COOH (0.06 ml) and CH_2Cl_2 (100 ml) was stirred at room temperature (3 h), poured into H_2O (100 ml) and extracted with CH_2Cl_2 (3 × 100 ml). Isolation of the product was conducted as above.

a) Preparation of quinolinequinone (3a-j)

6-Chloro-3-methyl-5,8-quinolinequinone (3a)

a) According to procedure B, 2,5-dichlorobenzoquinone (**2a**) (354 mg; 2.00 mmol) and 1-dimethylamino-3-methyl-1-azabuta-1,3-diene (**1a**) (112 mg; 1.00 mmol) gave quinolinequinone (**3a**) (148 mg; 71%), mp 177°C (decomp.) (from $CHCl_3$-hexanes); ir ν_{max} (KBr) 1670, 1655, 1590 cm^{-1}; ^{1}H-nmr (300 MHz, $CDCl_3$) δ 2.55 (3H, s, 3-CH_3), 7.35 (1H, s, 7-H), 8.27 (1H, d, J = 2.3 Hz, 4-H), 8.88 (1H, d, J = 2.1 Hz, 2-H); ms (m/z) 209/207 (100) (M^+). Anal. Calcd for $C_{10}H_6NO_2Cl$: C, 57.85; H, 2.91; N, 6.75. Found: C, 57.98; H, 2.88; N, 6.61.

b) Procedure C gave a 15% yield (31 mg) of quinone (**3a**).

7-Chloro-3-methyl-5,8-quinolinequinone (3b)

a) Application of procedure B to 2,6-dichlorobenzoquinone (**2b**) (354 mg; 2.00 mmol) and azadiene (**1a**) (112 mg; 1.00 mmol) provided quinolinequinone (**3b**) (115 mg; 56%), mp 145°C (decomp.) (from $CHCl_3$-hexanes); ir ν_{max} (KBr) 1685, 1660, 1590 cm^{-1}; ^{1}H-nmr (300 MHz, $CDCl_3$) δ 2 52 (3H, s, 3-CH_3), 7.24 (1H, s, 6-H), 8.16 (1H, d, J = 2.1 Hz, 4-H), 8.85 (1H, d, J = 2.0 Hz, 2-H); ms (m/z) 209/207 (100) (M^+). Anal. Calcd for $C_{10}H_6NO_2Cl$: C, 57.85; H, 2.91; N, 6.75. Found: C, 57.59; H, 2.80; N, 6.50.

b) A 32% yield (66 mg) of quinone (**3b**) was observed with the use of procedure C.

6-Methoxy-3-methyl-5,8-quinolinequinone (3c)

The cycloaddition of azadiene (**1a**) (123 mg; 1.10 mmol) to 2-chloro-5-methoxybenzoquinone[20] (**2c**) (173 mg; 1.00 mmol) using procedure A [CH_2Cl_2 (20 ml); 6 h] provided quinone (**3c**) (148 mg; 73%), mp 224°C (decomp.) (from MeOH); ir ν_{max} (KBr) 1685, 1665, 1610, 1590 cm^{-1}; ^{1}H-nmr (300 MHz, $CDCl_3$) δ 2.48 (3H, s, 3-CH_3), 3.90 (3H, s, 6-OCH_3), 6.28 (1H, s, 7-H), 8.19 (1H, d, J = 2.1 Hz, 4-H), 8.80 (1H, d, J = 1.9 Hz, 2-H); ms (m/z) 203 (100) (M^+); HRms calcd for $C_{11}H_9NO_3$: 203.0582, found: 203.0574.

7-Methoxy-3-methyl-5,8-quinolinequinone (3d)

In an experiment similar to the foregoing, 2-chloro-6-methoxybenzoquinone[20] (**2d**) led to the formation of *quinolinequinone* (**3d**) (148 mg; 73%) which sublimes at ~ 220°C (from MeOH); ir ν_{max} (KBr) 1695, 1640, 1605, 1582 cm^{-1}; ^{1}H-nmr (300 MHz, $CDCl_3$) δ 2.52 (3H, s 3-CH_3), 3.93 (3H, s, 7-OCH_3), 6.21 (1H, s, 6-H), 8.18 (1H, d, J = 2.1 Hz, 4-H), 8.82 (1H, d, J = 2.2 Hz, 2-H); ms (m/z) 203 (100) (M^+). Anal. Calcd for $C_{11}H_9NO_3$: C, 65.02; H, 4.46; N, 6.89. Found: C, 65.35; H, 4.50; N, 6.81.

6-Methoxy-4-methyl-5,8-quinolinequinone (3e)

2-Chloro-5-methoxybenzoquinone[20] (**2c**) (173 mg; 1.00 mmol) and 1-azapentadiene (**1b**) (123 mg; 1.10 mmol), by application of procedure A [CH_2Cl_2 (20 ml); 5 d], afforded quinolinequinone (**3e**) (86 mg; 42%), mp 205°C (decomp.) (from MeOH); ir ν_{max} (KBr) 1680, 1620, 1582 cm^{-1}; ^{1}H-nmr (200 MHz, $CDCl_3$) δ 2.76 (3H, s, 4-CH_3), 3.90 (3H, s, 6-OCH_3), 6.27 (1H, s, 7-H), 7.39 (1H, d, J = 5.1 Hz, 3-H), 8.78 (1H, d, J = 5.0 Hz); ms (m/z) 203 (100) (M^+); HRms calcd for $C_{11}H_9NO_3$: 203.0582, found: 203.0585.

7-Methoxy-4-methyl-5,8-quinolinequinone (3f)

The reaction of 2-chloro-6-methoxybenzoquinone[20] (**2d**) (173 mg; 1.00 mmol) and 1-dimethylamino-1-azapenta-1,3-diene (**1b**) (123 mg, 110 mmol) as in procedure A in CH_2Cl_2 (20 ml) (4 d) provided quinolinequinone (**3f**) (35 mg; 17%), mp 181-182°C (decomp.) (from MeOH); ir ν_{max} (KBr) 1700, 1620, 1500 cm^{-1}; ^{1}H-nmr (200 MHz, $CDCl_3$) δ 2.76 (3H, s, 4-CH_3), 3.88 (3H, s, 7-OCH_3), 6.13 (1H, s, 6-H), 7.40 (1H,

d, J = 4.6 Hz, 3-H), 8.76 (1H, d, J = 4.6 Hz, 2-H); ms (m/z) 203 (39) (M^+), 69 (100). Anal. Calcd for $C_{11}H_9NO_3$: C, 65.02; H, 4.46; N, 6.89. Found: C, 65.15; H, 4.41; N, 6.95.

6-Chloro-5,8-quinolinequinone (3g)

a) Procedure B (1.5 h), when applied to 2,5-dichlorobenzoquinone (**2a**) (354 mg; 2.00 mmol) and azadiene (**1c**) (98 mg; 1.00 mmol) provided quinoline-quinone (**3g**) (66 mg; 36%), mp 176-178°C (decomp.) (from $CHCl_3$ - hexanes) [lit.,[7] mp ~ 180°C (decomp.)].

b) By application of procedure A, the yield of quinone (**3g**) is increased to 50% (98 mg).

7-Chloro-5,8-quinolinequinone (3h)

As in the foregoing case, 2,6-dichlorobenzoquinone (**2b**) (354 mg; 2.00 mmol) and 1-dimethylamino-1-azabuta-1,3-diene (**1c**) (98 mg; 1.00 mmol) gave quinolinequinone (**3h**) (49 mg; 26%), mp 167-168°C (decomp.) [lit.,[7] mp ~ 173.5-174.5°C (decomp.)] (from $CHCl_3$ - hexanes).

6-Methoxy-5,8-quinolinequinone (3i)

The use of procedure A (CH_2Cl_2, 2 ml) with 2-chloro-5-methoxybenzoquinone[20] (**2c**) (173 mg; 1.00 mmol) and azadiene (**1c**) (108 mg; 1.10 mmol) afforded, in **3d**, quinolinequinone (**3i**) (67 mg; 35%), which sublimes at ~ 229°C (from MeOH) [lit.,[9] mp 245°C (decomp.)].

7-Methoxy-5,8-quinolinequinone (3j)

As in the preceding paragraph 2-chloro-6-methoxybenzoquinone[20] (**1d**) (173 mg; 1.00 mmol) and azadiene (**1c**) (108 mg; 1.10 mmol) in CH_2Cl_2 (2 ml) for 4 d produced quinolinequinone (**3j**) (32 mg; 17%), which sublimes at ~ 231°C (from MeOH); ir ν_{max} (KBr) 1690, 1645, 1600, 1582 cm^{-1}; ^{1}H-nmr (200 MHz, $CDCl_3$) δ 3.94 (3H, s, 7-OCH_3), 6.24 (1H, s, 6-H), 7.68 (1H, dd, J = 4.6; 7.9 Hz, 3-H), 8.41 (1H, dd, J = 1.7; 7.9 Hz, 4-H), 9.01 (1H, dd, J = 1.7; 4.6 Hz, 2-H); ^{13}C-nmr (75.5 MHz, $CDCl_3$) δ 56.7 (OCH_3), 109.4 (6-H), 128.0 (3-C), 129.1 (4a-C), 134.3 (4-C), 146.9 (8a-C), 154.3 (2-C), 161.0 (7-C), 178.2 (5-C), 183.5 (8-C); ms (m/z)

189 (87) (M^+), 103 (100); HRms calcd for $C_{10}H_7NO_3$: 189.0426, found: 189.0412.

b) Preparation of 5,10-benzo[*g*]quinolinequinone (5a, b - 6a, b)

6-Hydroxy-3-methyl-5,10-benzo[*g*]quinolinequinone (5a)

Application of procedure A [CH_2Cl_2 (20 ml); 5 d] to 2-chlorojuglone[21] (**4a**) (209 mg; 1.00 mmol) and 1-azadiene (**1a**) (123 mg; 1.10 mmol) gave benzo[*g*]quinolinequinone (**5a**) (160 mg; 67%), mp 258-259°C (from AcOEt - hexanes) (lit.,[2] mp 261-263°C).

6-Methoxy-3-methyl-5,10-benzo[*g*]quinolinequinone (5b)

In a reaction similar to the foregoing [CH_2Cl_2 (20 ml); 48 h], 2-chlorojuglone 5-methyl ether (**4b**) (223 mg; 1.00 mmol) and azadiene (**1a**) (123 mg; 1.10 mmol) provided benzo[*g*]quinolinequinone (**5g**) (177 mg; 70%), mp 194-196°C (from MeOH) (lit.,[2] mp 198-200°C).

9-Hydroxy-3-methyl-5,10-benzo[*g*]quinolinequinone (6a)

The addition of 1-azadiene (**1a**) (123 mg; 1.10 mmol) to 3-chlorojuglone[21] (**4c**) (209 mg; 1.00 mmol) by procedure A [CH_3CN (20 ml); 5 d] afforded benzo[*g*]quinolinequinone (**6a**) (220 mg; 92%), mp 217-218°C (from EtOH) (lit.,[2] mp 225-226°C).

9-Methoxy-3-methyl-5,10-benzo[*g*]quinolinequinone (6b)

As per procedure A, [CH_3CN (20 ml); 72 h], 3-chlorojuglone 5-methyl ether (**4d**) (223 mg; 1.00 mmol) and 1-azadiene (**1a**) (123 mg; 1.10 mmol) gave benzo[*g*]quinolinequinone (**6b**) (168 mg; 66%), mp 184°C (decomp.) (from MeOH) (lit.,[2] mp 184-185°C).

II Substitution of chloroquinolinequinones

7-[2-Methoxycarbonylphenoxy]-5,8-quinolinequinone (7a)

To a solution of methyl salicylate (109 mg; 1.30 mmol) in DMF (20 ml) containing 50% KF on Celite (175

mg; 1.50 mmol) was added (30 min; room temperature) 7-chloroquinolinequinone (**3h**) (194 mg; 1.00 mmol) in the same solvent (40 ml). The mixture was stirred at room temperature (45 min), then at 106°C (4 h), cooled and poured into water (400 ml) and sat. brine (200 ml). The ether extracts (3 × 150 ml) were washed with brine (6 × 250 ml), dried over $MgSO_4$ and evaporated. Purification of the residue by flash chromatography (CH_2Cl_2 - AcOEt, 10:1) provided quinolinequinone (**7a**) (212 mg; 67%), mp 167°C (from C_6H_6 - hexanes); ir ν_{max} (KBr) 1718, 1700, 1645, 1610, 1595, 1575, 1480 cm^{-1}; ^{1}H-nmr (300 MHz, $CDCl_3$) δ 3.74 (3H, s, 2'-CO_2CH_3), 5.82 (1H, s, 6-H), 7.17-7.63 (3H, m, 4',5',6'-H), 7.68 (1H, dd, J = 4.5; 8.0 Hz, 3-H), 8.05 (1H, dd, J = 1.7; 7.8 Hz, 3'-H), 8.37 (1H, dd, J = 1.8; 7.8 Hz, 4-H), 9.03 (1H, dd, J = 1.6; 4.6 Hz, 2-H); ms (m/z) 309 (100) (M^+). Anal. Calcd for $C_{17}H_{11}NO_5$: C, 66.01; H, 3.59; N, 4.53. Found: C, 66.27; H, 3.50; N, 4.57.

6-[2-Methoxycarbonylphenoxy]-5,8-quinolinequinone (8a)

As in the preceding paragraph, the reaction of 6-chloroquinolinequinone (**3g**) (97 mg; 0.50 mmol) with methyl salicylate (95 mg; 0.60 mmol) led to quinolinequinone (**8a**) (67 mg; 44%), mp 155°C (from C_6H_6 -hexanes); ir ν_{max} (KBr) 1715, 1685, 1650, 1615, 1598, 1570, 1565, 1450 cm^{-1}; ^{1}H-nmr (300 MHz, $CDCl_3$) δ 3.70 (3H, s, 2'-CO_2CH_3), 5.88 (1H, s, 7-H), 7.17-7.63 (3H, m, 4',5',6'-H), 7.67 (1H, dd, J = 4.9; 8.0 Hz, 3-H), 8.06 (1H, dd, J = 1.7; 7.8 Hz, 3'-H), 8.51 (1H, dd, J = 1.7; 8.0 Hz, 4-H), 9.01 (1H, dd, J = 1.5; 4.7 Hz, 2-H); ms (m/z) 309 (94) (M^+), 222 (100). Anal. Calcd for $C_{17}H_{11}NO_5$: C, 66.01; H, 3.59; N, 4.53. Found: C, 66.22; H, 3.49; N, 4.59.

7-[*N*-Mesyl-2-methoxycarbonylanilino]-5,8-quinolinequinone (7b)

To a suspension of 50% CsF on Celite (456 mg; 1.50 mmol) and 18-crown-6 (26 mg; 0.10 mmol) in DMF (10 ml) at 45°C was added a solution of 7-chloro-5,8-quinolinequinone (**3h**) (194 mg; 1.00 mmol) and methyl *N*-mesylanthranilate (229 mg; 1.00 mmol) in the same solvent (10 ml). The mixture was stirred at the same temperature (2 h), cooled, poured into saturated brine (100 ml) and extracted with ether (3 × 100 ml). After washing the organic extracts with brine (150 ml), drying over $MgSO_4$ and evaporating, the residue was

purified by flash chromatography (CH_2Cl_2 - AcOEt 10:1) and yielded quinolinequinone (**7b**) (143 mg; 37%), mp 193.0-193.5°C (from C_6H_6 - hexanes); ir ν_{max} (KBr) 1725, 1680, 1670, 1603, 1575, 1480 cm^{-1}; ^{1}H-nmr (300 MHz, $CDCl_3$) δ 3.55 (3H, s, *N*-SO_2CH_3), 3.86 (3H, s, 2'-CO_2CH_3), 6.64 (1H, s, 6-H), 7.50-7.66 (3H, m, 4',5',6'-H), 7.69 (1H, dd, J = 4.7; 8.0 Hz, 3-H), 7.96 (1H, dd, J = 1.7; 7.6 Hz, 3'-H), 8.36 (1H, dd, J = 1.7; 7.7 Hz, 4-H), 9.05 (1H, dd, J = 1.7; 4.7 Hz, 2-H); ms (m/z) 386 (1) (M^+), 307 (100). Anal. Calcd for $C_{18}H_{14}N_2O_6S$: C, 55.95; H, 3.65; N, 7.25. Found: C, 56.17; H, 3.60; N, 7.13.

6-[*N*-Mesyl-2-methoxycarbonylanilino]-5,8-quinolinequinone (8b)

In an experiment analogous to the foregoing one, 6-chloroquinolinequinone (**3g**) (194 mg; 1.00 mmol) and methyl *N*-mesylanthranilate (229 mg; 1.00 mmol) gave quinolinequinone (**8b**) (50 mg; 13%), mp 180.0-180.5°C (from C_6H_6 - hexanes); ir ν_{max} (KBr) 1720, 1695, 1650, 1595, 1570, 1480 cm^{-1}; ^{1}H-nmr (300 MHz, $CDCl_3$) δ 3.53 (3H, s, *N*-SO_2CH_3), 3.84 (3H, s, 2'-CO_2CH_3), 6.63 (1H, s, 7-H), 7.49-7.67 (3H, m, 4',5',6'-H), 7.70 (1H, dd, J = 4.7; 7.8 Hz, 3-H), 7.99 (1H, dd, J = 1.80; 7.6 Hz, 3'-H), 8.47 (1H, dd, J = 1.7; 7.8 Hz, 4-H), 9.04 (1H, dd, J = 1.7; 4.8 Hz, 2-H); ms (m/z) 386 (4) (M^+), 307 (100). Anal. Calcd for $C_{18}H_{14}N_2O_6S$: C, 55.95; H, 3.65; N, 7.25. Found C, 56.09, H, 3.65; N, 7.28.

III Cycloadditions to chloroquinolinequinones

6-Hydroxy-8-methoxy-5,10-benzo[*g*]quinolinequinone (10)

To 6-chloroquinolinequinone (**3g**) (194 mg; 1.00 mmol) in dry CH_2Cl_2 (6 ml) was added at 0°C 1,3-dimethoxy-1-trimethylsiloxybuta-1,3-diene (**9**) (300 mg; 1.50 mmol). The mixture was stirred at room temperature (4 h), concentrated under vacuum, dissolved in THF (20 ml), cooled to 0°C and diluted with conc. HCl. After stirring at room temperature (24 h), the solution was extracted with AcOEt (3 × 50 ml) and the extracts washed with H_2O (3 × 50 ml). Flash chromatography (AcOEt) of the crude product on deactivated silica gel [2% $(CO_2H)_2$] gave azaanthraquinone (**10**) (227 mg; 89%), (from AcOEt - hexanes); ir ν_{max} (KBr) 1680, 1620 cm^{-1}; ^{1}H-nmr (200 MHz, $CDCl_3$) δ 3.96 (3H, s, 8-OCH_3), 6.76 (1H, d, J = 2.6 Hz, 7-H), 7.49 (1H, d, J = 2.6 Hz, 9-H), 7.73 (1H, dd, J = 4.4; 7.9 Hz, 3-H), 8.64 (1H, dd, J = 1.8; 8.0 Hz, 4-H), 9.09 (1H, dd,

J = 1.6; 4.7 Hz, 2-H), 12.60 (1H, s, 6-OH); ms (m/z) 255 (60) (M^+), (212) (100); HRms calcd for $C_{14}H_9NO_4$: 255.0532, found: 255.0523.

9-Hydroxy-7-methoxy-5,10-benzo[*g*]quinolinequinone (11)

In a reaction similar to the preceding one, 7-chloroquinolinequinone (**3h**) (194 mg; 1.00 mmol) and diene (**9**) (300 mg; 1.50 mmol) gave azaanthraquinone (**11**) (234 mg; 91%), (from AcOEt - hexanes); ir ν_{max} (KBr) 1670, 1630 cm^{-1}; ^{1}H-nmr (200 MHz, $CDCl_3$) δ 3.95 (3H, s, 7-OCH_3), 6.76 (1H, d, J = 2.6 Hz, 8-H), 7.38 (1H, d, J = 2.6 Hz, 6-H), 7.71 (1H, dd, J = 4.4; 7.9 Hz, 3-H), 8.58 (1H, dd, J = 1.6; 7.9 Hz, 4-H), 9.10 (1H, dd, J = 1.4; 4.4 Hz, 2-H), 12.81 (1H, s, 9-OH); ms (m/z) 255 (64) (M^+), 212 (100); HRms calcd for $C_{14}H_9NO_4$: 255.0532, found: 255.0539.

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