Pergamon

Tetrahedron, Vol. 53, No. 33, pp. 11465-11480, 1997

0040-4020/97 $17.00 + 0.00

PII: S0040-4020(97)00726-6

Hetero Diels-Alder Reactions of 4,5,8(1*H*)-Quinolinetriones

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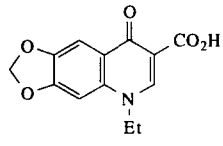
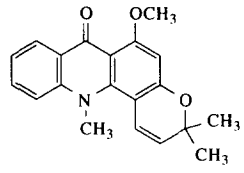
Abstract: *N*-substituted 4,5,8(1*H*)-quinolinetriones react with 1-dimethylamino-1-azadienes giving 1,8-diazaanthracene-4,9,10-triones or 9,10-dihydroxy-1,8-diazaanthracene-4,9,10-triones as the main reaction products. The outcome of the reaction depends on the nature of the *N*-substituent on the quinone and on the position of substituents on the azadiene. The regioselectivity of the cycloadditions was high, although lower than in the related reactions of 2,5,8(1*H*)-quinolinetriones previously studied by our group, leading to the isolation of small amounts of 1,5-diazaanthracene-4,9,10-triones. By manipulation of the experimental conditions, the course of the reaction can be diverted to give furo[2,3-*f*]quinolines through a multi-step, polar [3+2] cycloaddition. © 1997 Elsevier Science Ltd.

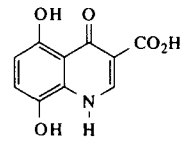
The 4(1*H*)quinolinone unit is present in several important types of compounds, the best known of which are the so-called 'quinolone' antibacterials (*e.g.* oxolinic acid).[1] Some natural products also bear this substructure. For example, several genera of plants belonging to the *Rutaceae* family contain acridine alkaloids like acromycine,[2] a substance with an unusually broad spectrum of antitumour activity.[3] Some marine natural products also contain a 4(1*H*)quinolinone moiety.[4] Among them, uranidine, from the sponge *Verongia aerophoba*,[5] and the cytotoxic plakinidine C,[6] isolated from sponges of the *Plakortis* genus, may be cited as examples. Several related compounds have been isolated from natural sources as 4-hydroxy tautomers; these include phomazarine[7] and meridine.[8]



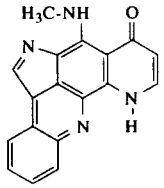
Oxolinic acid



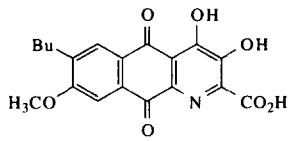
Acromycine



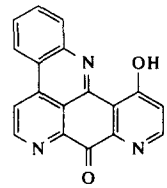
Uranidine



Plakinidine C



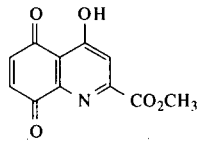
Phomazarine



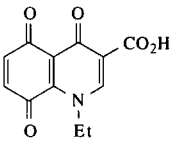
Meridine

In view of these precedents, the Diels-Alder chemistry of 4,5,8(1*H*)-quinolinetriones or their 4-hydroxy tautomers appears as an interesting field of study. However, the literature on this topic is very scarce and often not encouraging. Thus, 2-methoxycarbonyl-4-hydroxy-5,8-quinolinequinone **1** gave only a 7 % yield of the expected cycloadduct with 1,3-cyclohexadiene, and none at all with 1,3-dimethoxy-1,3-cyclohexadiene.[9,10] The only 4,5,8-quinolinetrione studied is this regard is compound **2**, which afforded good yields of Diels-Alder adducts with four different dienes, although their symmetry did not allow regiochemical studies.[11] To our knowledge, reactions between 4,5,8-quinolinetriones and heterodienes are unknown in the literature.

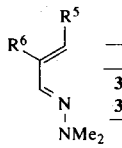
Due to this lack of precedent and to our interest[12] in the hetero Diels-Alder reaction between 1-dimethylamino-1-azadienes[13] and heterocyclic quinones, we decided to examine the reactivity of crotonaldehyde dimethylhydrazone **3a** and methacrolein dimethylhydrazone **3b**[14] towards quinones **4**.



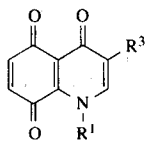
1



2

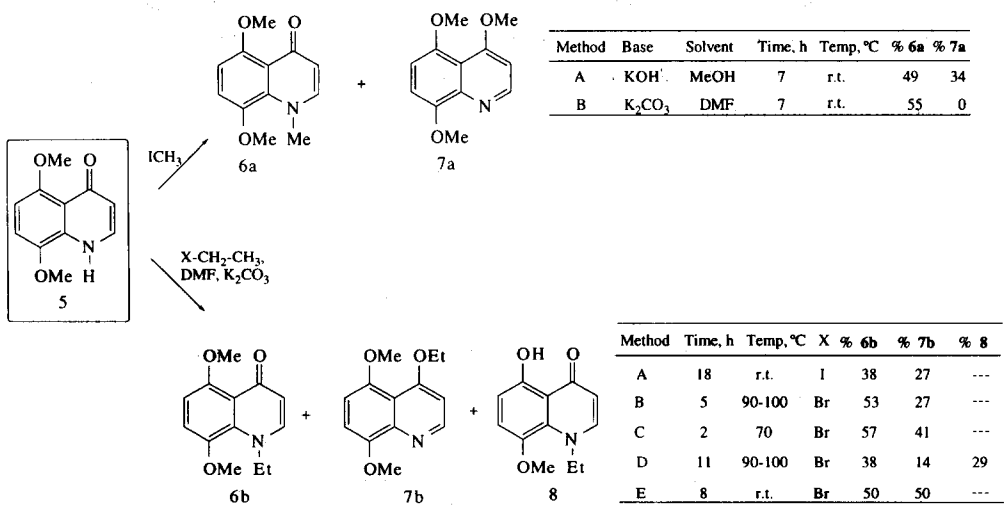


	R^5	R^6
3a	CH_3	H
3b	H	CH_3



	R^1	R^3
4a	CH_3	H
4b	Et	H
4c	CH_3	CO_2Et

The synthesis of quinones **4a,b** is summarized in Scheme 1. *N*-alkylation of the known[15] 5,8-dimethoxy-4(1*H*)-quinolinone **5**, although complicated by competing reaction of the C-4 oxygen,[16] afforded the desired compounds **6a** and **6b**, together with **7a** and **7b**. In one of the experiments, a small amount of the O_5-demethylated derivative **8** was isolated.

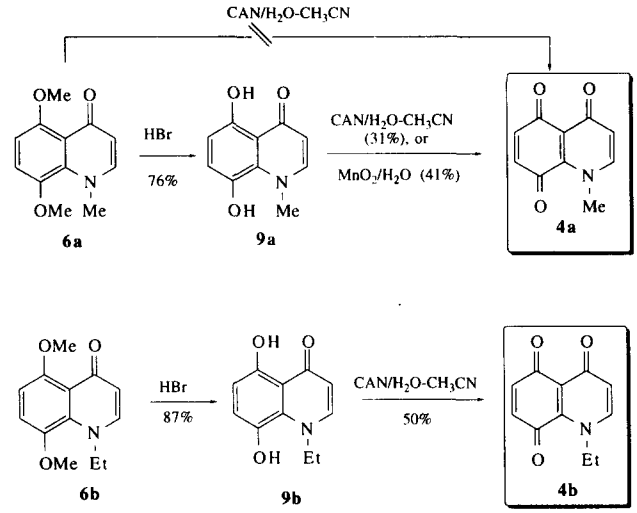


Method	Base	Solvent	Time, h	Temp, °C	% 6a	% 7a
A	KOH	MeOH	7	r.t.	49	34
B	K_2CO_3	DMF	7	r.t.	55	0

Method	Time, h	Temp, °C	X	% 6b	% 7b	% 8
A	18	r.t.	I	38	27	---
B	5	90-100	Br	53	27	---
C	2	70	Br	57	41	---
D	11	90-100	Br	38	14	29
E	8	r.t.	Br	50	50	---

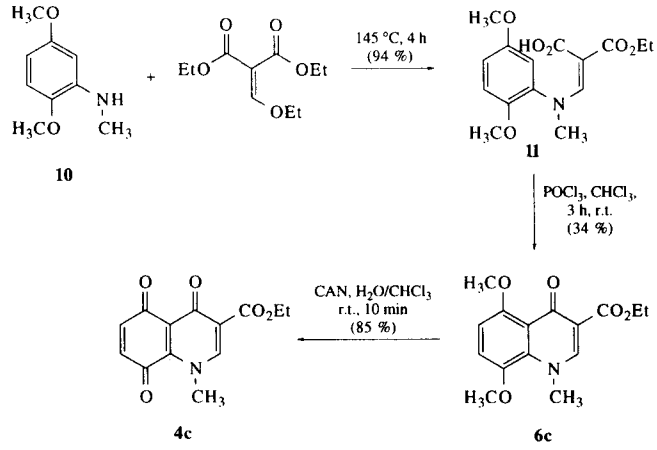
Scheme 1

Attempted direct oxidative demethylation of **6a** with cerium ammonium nitrate was unsuccessful, and therefore it had to be demethylated with refluxing aqueous hydrobromic acid to **9a** prior to oxidation to quinone **4a**. **6b** was also transformed into quinone **4b** through a two-step demethylation-oxidation sequence (Scheme 2).



Scheme 2

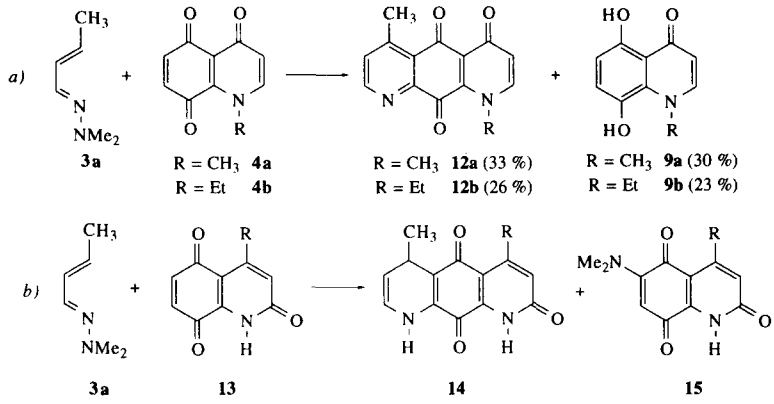
For the preparation of quinone **4c**, *N*-methyl-2,5-dimethoxyaniline **10**[17] was treated with ethyl ethoxymethylenemalonate at 145 °C for 4 h to give compound **11**, which was cyclized to **6c** by exposure to phosphorous oxychloride. Finally, oxidative demethylation of **6c** with cerium ammonium nitrate gave **4c** (Scheme 3).



Scheme 3

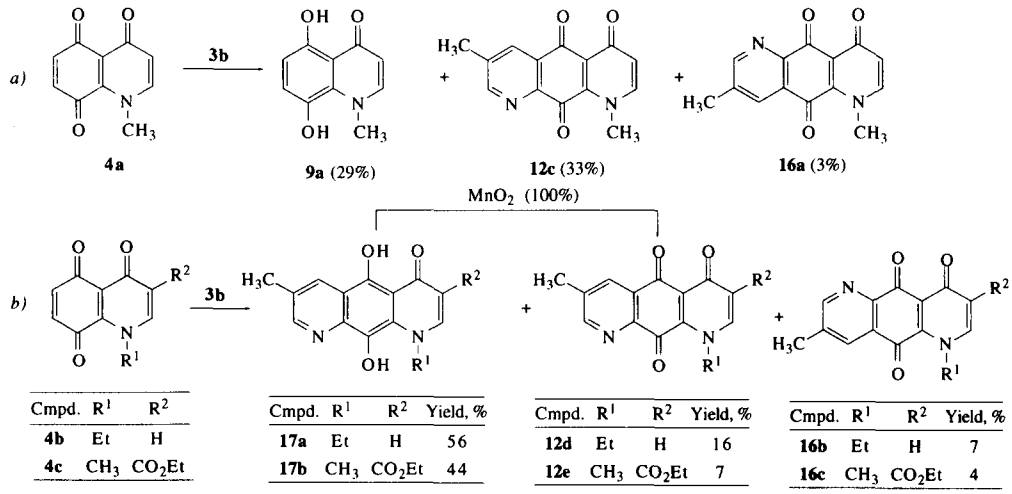
The behaviour of quinones **4** in their hetero Diels-Alder reactions differed considerably from the one observed in 2,5,8-quinolinetriones. Thus, treatment of compounds **4a,b** with crotonaldehyde dimethyl-

hydrazone gave equimolecular mixtures of the fully aromatized Diels-Alder adducts **12a,b** and hydroquinones **9a,b** from reduction of the starting quinones, while the vinylogous 2,5,8(1*H*)-quinolinetriones **13**, under the same conditions, normally yield dihydro derivatives **14**, together with the secondary products **15** from addition of dimethylamine to the starting quinone (Scheme 4).[12]



Scheme 4

The reactivity of quinones **4** towards methacrolein dimethylhydrazone (**3b**) also showed some interesting peculiarities. Thus, while the 1-methyl quinone **4a** gave a mixture of the corresponding hydroquinone **9a** and the two regioisomeric, aromatic Diels-Alder adducts **12c** and **16a** in a 11:1 ratio (Scheme 5a), quinones **4b** and **4c** exhibited a different behaviour. When they were submitted to the same tratment, the major products were the tricyclic hydroquinones **17a** and **17b**, which were accompanied by small amounts of their oxidized forms (compounds **12d** and **12e**) and their 1,5-diaza- regioisomers (**16b** and **16c**, respectively) Tricyclic hydroquinones equivalent to **17** have never been isolated in similar reactions of 2,5,8-quinolinetriones.[12] As expected,[18] these reactions required shorter reaction times than those performed with azadiene **3b**.



Cmpd.	R^1	R^2
4b	Et	H
4c	CH_3	CO_2Et

Cmpd.	R^1	R^2	Yield, %
17a	Et	H	56
17b	CH_3	CO_2Et	44

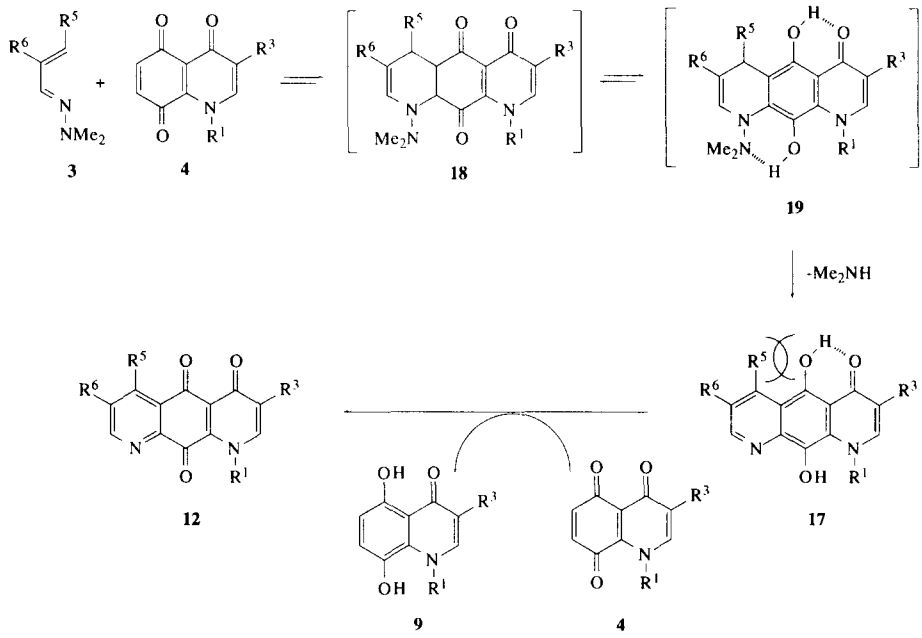
Cmpd.	R^1	R^2	Yield, %
12d	Et	H	16
12e	CH_3	CO_2Et	7

Cmpd.	R^1	R^2	Yield, %
16b	Et	H	7
16c	CH_3	CO_2Et	4

Scheme 5

Finally, compounds **16a** and **16b** were quantitatively oxidized to **11d** and **11e**, respectively, by treatment with a suspension of manganese dioxide in chloroform (Scheme 5).

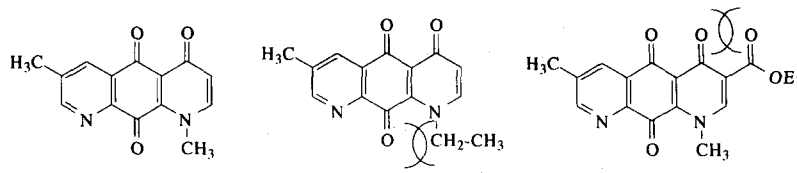
A tentative explanation for the facts described above can be found in Scheme 6. Intermediate **18** formed as the primary Diels-Alder adduct would tautomerize to **19**, a step favoured by intramolecular hydrogen bonding between both hydroxyls. Elimination of dimethylamine from **19** would lead to compounds **17**, which, in the cases where $R^5 = CH_3$, would not be stabilized by intramolecular hydrogen bonding because steric interactions between R^5 and the C_{10}-OH group would force this group out of planarity. This would favour their oxidation to the corresponding quinones **12**, with the starting quinone **4** acting as the oxidant and therefore leading to hydroquinones **9** as a by-product in yields that are similar to those of **12**.



Scheme 6

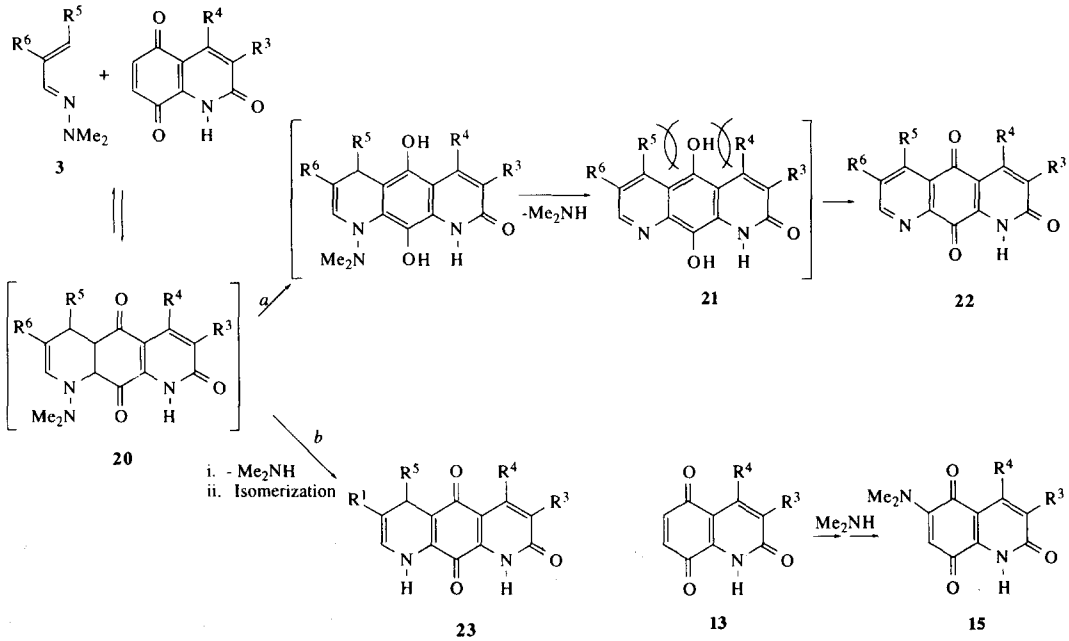
In the cases where $R^5 = H$ (*i.e.*, in the reactions starting from methacrolein dimethylhydrazone **3b**), hydrogen bonding would stabilize intermediates **17**, leading to their isolation as the major products. The isolation in these reactions of minor quantities of compounds **12**, not accompanied by equivalent amounts of **9**, can be explained by partial oxidation of **17** by the air/dimethylamine system. Indeed, we have observed in a separate experiment that compound **17a** is rapidly oxidized to the corresponding quinone (**12c**) upon exposure to an aqueous solution of dimethylamine at room temperature.

The exceptional behaviour observed in the reaction between quinone **4a** and azadiene **3b** shows that the corresponding intermediate **17** is easier to oxidize than its analogues derived from quinones **4b** or **4c**. This fact can be correlated with the experimental half-wave potentials of the oxidized Diels-Alder adducts **12c-e** [$E_{1/2}$ (**12e**) < $E_{1/2}$ (**12d**) < $E_{1/2}$ (**12c**)],[19] and may be ascribed to steric effects in quinones **12d** and **12e**:



12c **12d** **12e**

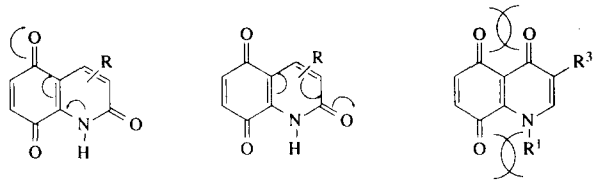
The differences found between the behaviours of compounds **4** and 2,5,8-quinolinetriones are also easily explained in terms of steric effects in reaction intermediates. Thus, if the latter compounds are 4-substituted, evolution of their primary hetero Diels-Alder adducts **20** by pathway *a* shown in Scheme 7 to compounds **21** (which are the counterparts of **17**) would be hampered by repulsive interactions between R_4 and C_{10}-OH. Therefore, the alternative pathway *b*, initiated by elimination of dimethylamine, is followed, leading to 5,8-dihydro derivatives **23** and also to compounds **15**, from addition of the liberated dimethylamine to the starting quinone. In other cases (*e.g.*, when R^4, R^5, or both, are hydrogen), pathway *a* is possible, but compounds **21** are less stable than **17** owing to lack of intramolecular hydrogen bonding and they can not be isolated because they are oxidized to **22**.



Scheme 7

The isolation of 1,5-diazaanthracene derivatives in the hetero Diels-Alder reactions of compounds **4**, albeit in small amounts, contrasts with the complete regioselectivity normally found in similar reactions of 2,5,8(1*H*)-quinolinetriones. In the latter case, this selectivity can be explained by the conjugation of the nitrogen atom with the C_5=O carbonyl, which leaves the C_6=C_7-C_8=O portion of the molecule as a relatively isolated enone system with its electrophilic end at C_6. Also, the electron-withdrawing effect of C_2=O is transmitted by conjugation to

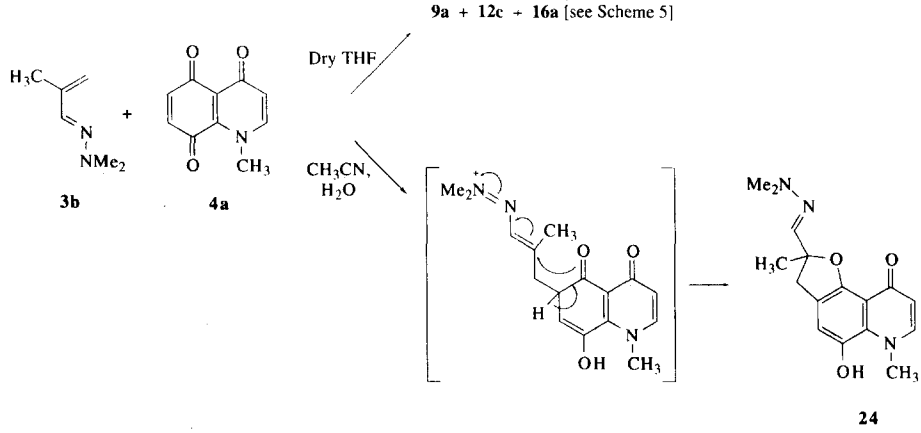
C_8=O, thereby increasing the electron defficiency at C_6. Both effects would be hampered in our 1-substituted 4,5,8-quinolinetrione systems **4**, since steric effects would prevent complete coplanarity of the system:



4

Finally, solvent effects in the hetero Diels-Alder reactions of quinones **4** were briefly examined. While the reaction between **4a** and azadiene **3b** in THF gave a mixture of hydroquinone **9a** and the expected 1,8-diaza- and 1,5-diaza cycloadducts **12a** and **16a** (see Scheme 5), when the same reagents were mixed in acetonitrile-water the only product isolated was the furo[2,3-*f*]quinoline derivative **24**; its regiochemistry was confirmed by a NOE experiment, which showed an enhancement of the *N*-methyl signal upon irradiation of the OH singlet.

The formation of **24** can be rationalized as the result of a conjugate addition of the more nucleophillic end of the azadiene (C-4) to C-6 of the quinone, followed by 5-*exo-trig* ring closure (Scheme 8). We had previously noted[12] a similar behaviour for 2,5,8(1*H*)-quinolinetriones bearing strong electron acceptors at C-3, and attributed it to stabilization of the intermediates of the [3 + 2] cycloaddition by the polar reaction environment.[20] Other authors have reported related cyclizations in the reactions of 1-dimethylamino-1-azadienes with quinones in cases when either the diene or the dienophile are very polarized, due to the presence of electron-releasing groups in the diene[21] or electron-withdrawing groups in the dienophile,[22] or to the addition of Lewis or Brönsted acids to the reaction medium.[23,24]



Scheme 8

EXPERIMENTAL

All reagents were of commercial quality (Aldrich, Fluka, SDS, Probus) and were used as received. Solvents (SDS, Scharlau) were dried and purified using standard techniques. The expression "petroleum ether" refers to the fraction boiling at 40-60 °C. Reactions were monitored by thin layer chromatography, on aluminium plates coated with silica gel with fluorescent indicator (Scharlau Cf 530 and Macherey-Nagel Alugram Sil G/UV_{254}). Separations by flash chromatography were performed on silica gel (SDS 60 ACC, 230-400 mesh and Scharlau Ge 048). Melting points were measured on a Reichert 723 hot stage microsope or in open capillary tubes using a Büchi inmersion apparatus, and are uncorrected. Infrared spectra were recorded on Perkin-Elmer 577 (dispersive) and Perkin Elmer Paragon 1000 (FT-IR) spectrophotometers, with solid compounds compressed into KBr pellets and liquid compounds placed between two NaCl disks. NMR spectra were obtained on Bruker AC-250 (250 MHz for ^1H, 63 MHz for ^{13}C) and Varian VXR-300 (300 MHz for ^1H, 75 MHz for ^{13}C) spectrometers (Servicio de Espectroscopía, Universidad Complutense), with $CDCl_3$ or DMSO-d_6 as solvents. Elemental analyses were determined by the Servicio de Microanálisis, Universidad Complutense, on a Perkin-Elmer 2400 CHN microanalyzer.

Alkylation of 5,8-dimethoxy-4(1*H*)-quinolinone 5.

a) Methylation

METHOD A. Methyl iodide (14.75 g, 103.9 mmol) was added to a suspension of compound **5**[14] (1.64 g, 7.99 mmol) and potassium hydroxide (2.67 g, 45.6 mmol) in methanol (15 ml). The suspension was stirred at room temperature for 7 h. Volatiles were evaporated *in vacuo*, and the solid mass obtained was suspended in 4*N* aqueous sodium hydroxide (20 ml) and extracted with chloroform (3 x 100 ml) . The combined organic layers were dried over sodium sulphate and evaporated, and the residue was chromatographed on silica gel eluting with 9:1 ethyl acetate-ethanol or 9:1 ethyl acetate-acetone, yielding 588 mg (34 %) of the *O*-methylated derivative **7a** and 857 mg (49 %) of the *N*-methylated derivative **6a**.

METHOD B. Methyl iodide (6.81 g, 48.0 mmol) was added to a mixture of compound **5** (820 mg, 4.0 mmol) and potassium carbonate (1.3 g, 9.4 mmol) in dimethylformamide (15 ml). After stirring for 7 h at room temperature, volatile compounds were removed *in vacuo*. The residue was dissolved in chloroform (50 ml) and washed with water (1 x 25 ml). The chloroform layer was dried over sodium sulphate and evaporated, and the residue was purified by chromatography on silica gel, eluting with a gradiente from ethyl acetate to neat ethanol. Yield, 480 mg (55 %) of compound **6a**.

Data for **6a**: Mp, 63 °C. IR (KBr): 1638 (C=O); 1587 (C=C); 1270 (OCH_3) cm^{-1}. ^1H-NMR (250 MHz, $CDCl_3$) δ: 7.18 (d, 1H, *J* = 7.7 Hz, H-2); 6.99 (d, 1H, *J* = 8.9 Hz, H-7); 6.62 (d, 1H, *J* = 8.9 Hz, H-6); 6.08 (d, 1H, *J* = 7.7 Hz, H-3) 3.91 and 3.78 (2 s, 6H, 2 OCH_3); 3.84 (s, 3H, N-CH_3). ^{13}C-NMR (63 MHz, $CDCl_3$): 178.20 (C-4); 154.36 (C-5); 144.62 (C-2); 143.76 (C-8); 134.92 (C-8a); 119.65 (C-4a); 115.00 (C-7); 112.13 (C-6); 104.79 (C-3); 56.98 and 56.58 (OCH_3); 46.68 (N-CH_3). Anal. calcd. for $C_{12}H_{13}NO_3$: C, 65.75; H, 5.93; N, 6.39. Found: C, 65.56; H, 5.91; N, 6.05.

Data for **7a**: Mp, 129 °C. Lit.[25] 143-145 °C. ^{13}C-NMR (63 MHz, $CDCl_3$) δ: 164.16 (C-4); 150.47 (C-2); 150.22 (C-5); 149.53 (C-8); 142.64 (C-8a); 114.36 (C-4a); 107.63 (C-3); 106.15 (C-7); 101.92 (C-6); 57.06, 56.17 and 56.15 (OCH_3).

b) Ethylation

METHOD A. To a solution of compound **5** (880 mg, 4.29 mmol) in dimethylformamide (15 ml) was added potassium carbonate (1.63 g, 11.80 mmol) and ethyl iodide (1.40 g, 8.58 mmol). The suspension was stirred at room temperature for 18 h. Volatile compounds were removed *in vacuo* and the residue was suspended in choloroform (50 ml) and washed with water (1 x 20 ml). The organic layers was dried over sodium sulphate and evaporated and the residue was chromatographed on silica gel, eluting with a gradient from ethyl acetate to acetone. Yield, 268 mg (27 %) of the *O*-ethylated derivative **7b** and 380mg (38 %) of the *N*-ethylated derivative **6b**.

METHOD B. To a solution of compound **5** (1.03 g, 5.0 mmol) in dimethylformamide (18 ml) was added potassium carbonate (690 mg, 5.0 mmol) and ethyl bromide (1.46 g, 13.38 mmol). The suspension was stirred at 90-100 °C for 5 h and worked up as in Method A, yielding 313 mg (27 %) of **7b** and 620 mg (53 %) of **6b**.

METHOD C. As in Method B, starting from 2.3 g (11.22 mmol) of **5**, 804 mg (6.08 mmol) of potassium carbonate and 4.35 g (38.9 mmol) of ethyl bromide and carrying out the reaction at 70 °C for 2 h. Yield, 1.07 g (41 %) of **7b** and 1.51 g (57 %) of **6b**.

METHOD D. As in Method B, starting from 205 mg (1.0 mmol) of **5**, 345 mg (2.49 mmol) of potassium carbonate and 357 mg (3.27 mmol) of ethyl bromide and carrying out the reaction at 90-100 °C for 11 h. Yield, 32 mg (14 %) of **7b**, 88 mg (38 %) of **6b** and 63 mg (29 %) of 1-ethyl-5-hydroxy-8-methoxy-4(1*H*)-quinolinone **8**.

METHOD E. As in Method B, starting from 1.435 g (7 mmol) of **5**, 2.544 g (18.4 mmol) of potassium carbonate and 1.53 g (14 mmol) of ethyl bromide and carrying out the reaction at room temperature for 8h. Yield, 814 mg (50 %) of **7b** and 811 mg (50 %) of **6b**.

Data for **6b**: Mp, 72 °C. IR (KBr): 1633 (C=O); 1567 (C=C); 1257 (OCH_3) cm^{-1}. ^{1}H-NMR (250MHz, $CDCl_3$) δ: 7.72 (d, 1H, *J* = 7.7 Hz, H-2); 6.97 (d, 1H, *J* = 9.0 Hz, H-7); 6.61 (d, 1H, *J* = 9.0 Hz, H-6); 6.11 (d, 1H, *J* = 7.7 Hz, H-3); 4.30 (q, 2H, *J* = 7 Hz, N-CH_2 CH_3); 3.82 and 3.80 (2s, 6H, 2 OCH_3); 1.26 (t, 3H, N-CH_2CH_3). ^{13}C-NMR (63 MHz, $CDCl_3$): 178.34 (C-4); 154.15 (C-5); 143.84 (C-2); 143.31 (C-8); 133.63 (C-8a); 119.78 (C-4a); 114.23 (C-7); 112.45 (C-6); 104.95 (C-3); 56.69 and 56.55 (-OCH_3); 53.14 (N-CH_2 CH_3); 16.09 (N-CH_2CH_3). Anal. calcd. for $C_{13}H_{15}NO_3$: C, 66.95; H, 6.43; N, 6.00. Found: C, 66. 66; H, 6.35; N, 6.14.

Data for **7b**: Mp, 121 °C. IR (KBr): 1260 (OCH_3) cm^{-1}. ^{1}H-NMR (250MHz, $CDCl_3$) δ: 8.71 (d, 1H, *J* = 5.5 Hz, H-2); 6.94 (d, 1H, *J* = 8.6 Hz, H-7); 6.80 (d, 1H, *J* = 8.6 Hz, H-6); 6.77 (d, 1H, *J* = 5.5 Hz, H-3); 4.21 (c, 2H, *J* = 6.9 Hz, O-CH_2CH_3); 4.02 and 3.89 (2s, 6H, 2 OCH_3); 1.57 (t, 3H, *J* = 6.9 Hz, O-CH_2CH_3). ^{13}C-NMR (63 MHz, $CDCl_3$): 163.29 (C-4); 150.39 (C-2); 150.34 (C-5); 149.66 (C-8); 142.76 (C-8a); 114.66 (C-4a); 107.48 (C-3); 106.97 (C-7); 102.50 (C-6); 64.49 (O-CH_2 CH_3); 57.36 and 56.03 (OCH_3); 14.46 (O-CH_2CH_3). Anal. calcd. for $C_{13}H_{15}NO_3$: C, 66.95; H, 6.43; N, 6.00. Found: C, 67.19; H, 6.26; N, 5.94.

Data for **8**: Mp > 250 °C. IR (KBr): 2900 (OH); 1640 (C=O); 1500 (C=C) cm^{-1}. ^{1}H-NMR (250MHz, $CDCl_3$) δ: 14.92 (s, 1H, OH); 7.39 (d, 1H, *J* = 7 Hz, H-2); 7.06 (d, 1H, *J* = 8.8 Hz, H-7); 6.62 (d, 1H, *J* = 8.8 Hz, H-6); 6.12 (d, 1H, *J* = 7 Hz, H-3); 4.43 (q, 2H, *J* = 7 Hz, N-CH_2CH_3); 3.83 (s, 3H, OCH_3); 1.36 (t, 3H, *J* = 7 Hz, N-CH_2CH_3). ^{13}C-NMR (63 MHz, $CDCl_3$) δ: 182.40 (C-4); 156.34 (C-5); 145.90 (C-2); 140.49 (C-8); 132.63 (C-8a); 117.83 (C-7); 115.73 (C-4a); 108.79 (C-3); 108.74 (C-6); 57.26 (OCH_3); 53.76 (N-CH_2CH_3); 16.57 (N-CH_2CH_3). Anal. calcd. for $C_{12}H_{13}NO_3$: C, 65.78; H, 5.93; N, 6.39. Found: C,

65.43; H, 5.92; N, 6.25.

Ethyl [*N*-(2,5-Dimethoxyphenyl)-*N*-methyl]aminomethylene Hydrogen Malonate (11).

A solution of compound **10**[16] (1.67 g, 10 mmol) and diethyl ethoxymethylenemalonate (2.162 g, 10 mmol) in xylene (20 ml) heated at 145 °C for 2 h while connected to a Vigreaux column in order to distil off the ethanol formed during the reaction. An additional portion of diethyl ethoxymethylenemalonate (2.162 g, 10 mmol) was added and distillation was continued for 4 h more. Xylene was evaporated *in vacuo* and the residue was purified by chromatography on silica gel, eluting with petroleum ether-ethyl ether (5:1). Yield, 2.90 g (94 %) of **10**. IR (KBr): 3019 (OH); 1682 (C=O); 1142.3 (N-CH_3) cm^{-1}. ^{1}H-NMR (250MHz, $CDCl_3$) δ: 7.55 (s, 1H, C*H*=C); 6.82 (d, 1H, *J* = 8.9 Hz, H-5); 6.72 (dd, 1H, *J* = 8.9 and 2.9 Hz, H-4); 6.65 (d, 1H, *J* = 2.9 Hz, H-3); 4.10 (q, 2H, *J* = 7.09 Hz, COO*CH*$_2$ CH_3); 3.77 and 3.70 (s, 6H, 2 OCH_3); 3.24 (s, 3H, N-CH_3); 1.18 (t, 3H, *J* = 7.09 Hz, $COOCH_2CH_3$). ^{13}C-NMR (63 MHz, $CDCl_3$) δ: 166.75 (CO); 153.24 (*C*H=C); 150.29 (C-3); 147.5 (C-5); 114 (C-2); 112.95 (C-4); 112.38 (C-6); 109.2 (C-1); 96.08 (CH=*C*); 65.53 (COO*CH*$_2$ CH_3); 59.67, 55.89 and 55.45 (N-CH_3 and OCH_3); 14.28 ($COOCH_2CH_3$). Anal. calcd. for $C_{15}H_{19}NO_6$: C, 58.28; H, 6.14; N, 4.53. Found: C, 58.26; H, 6.12; N, 4.11.

Ethyl 1-methyl-5,8-dimethoxy-4-oxo-1,4-dihydroquinoline-3-carboxylate (6c).

To a refluxing solution of compound **11** (1.191 g, 3.85 mmol) in chloroform (1 ml) was slowly added a solution of freshly distilled phosphorous oxychloride (1.675 g, 10.92 mmol) in chloroform (1 ml) over 10 min. The solution was refluxed for 3 h and evaporated *in vacuo*. To the residue, cooled in an ice bath, was added ice (3 g) and 20 ml of 10 % aqueous sodium carbonate, and pH was finally adjusted to 8-9 with solid sodium bicarbonate (1.2 g). This aqueous solution was extracted with dichloromethane (5 x 50 ml), and the combined organic layers were dried over sodium sulphate and evaporated. The residue was purified by chromatography on silica gel, eluting with ethyl acetate. Yield, 373 mg (34 %) of compound **6c**. Mp, 91 °C. IR (KBr): 1720 (COOEt); 1632 (CO) cm^{-1}. ^{1}H-NMR (250MHz, $CDCl_3$) δ: 8.12 (s, 1H, H-2); 7.02 (d, 1H, *J* = 9.1 Hz, H-7); 6.71 (d, 1H, *J* = 9.1 Hz, H-6); 4.20 (q, 2H, *J* = 7.1 Hz, COO*CH*$_2$ CH_3); 3.96 (s, 3H, N-CH_3); 3.77 (s, 6H, -OCH_3); 1.25 (t, 3H, *J* = 7.1 Hz, $COOCH_2CH_3$). ^{13}C-NMR (63 MHz, $CDCl_3$): 175.16 (C-4); 165.43 (COOEt); 154.48 (C_5); 151.17 (C-2); 144.09 (C-8a); 133.02 (C-8); 120.90 (C-7); 116.22 (C-4a); 111.06 (C-3); 108.48 (C-6); 60.67 ($COOCH_2CH_3$). Anal. calcd. for $C_{15}H_{17}NO_5$: C, 61.88; H, 5.84; N, 4.81. Found: C, 61. 66; H, 5.35; N, 5.14.

1-Alkyl-5,8-dihydroxy-4(1*H*)-quinolinones 9. General procedure.

A solution of the suitable 5,8-dimethoxy-4 (1*H*)-quinolinone **6** in 40 % aqueous hydrobromic acid (20 ml) was refluxed for 24 h in a bath at 120 °C. The reaction mixture was cooled and diluted with water (20 ml) and extracted with ethyl acetate (10 x100 ml). The aqueous phase was neutralized with NaOH 1*N* and extracted again with ethyl acetate (10 x 100 ml). The combined organic layers were dried over sodium sulphate and evaporated, and the residue was crystallized from chloroform-ethyl acetate.

5,8-Dihydroxy-1-methyl-4 (1*H*)-quinolinone **9a**

Starting from compound **6a** (462 mg, 2.10 mmol), a yield of 307 mg (76 %) of **9a** was obtained. Mp, 260 °C. IR (KBr): 3417(OH); 1636 (C=O); 1574 (C=C) cm^{-1}. ^{1}H-NMR (250MHz, d_6-DMSO) δ: 14.53 and 9.50

(2s, 2H, 2 OH); 7.89 (d, 1H, J = 7.5 Hz, H-2); 7.02 (d, 1H, J = 8.6 Hz, H-7); 6.47 (d, 1H, J = 8.6 Hz, H-6); 6.01 (d, 1H, J = 7.5 Hz, H-3); 4.10 (s, 3H, N-CH_3). ^{13}C-NMR (63 MHz, d_6-DMSO): 181.38 (C-4); 153.91 (C-5); 148.30 (C-2); 138.40 (C-8); 130.62 (C-8a); 120.49 (C-7); 114.87 (C-4a); 108.51 (C-3); 106.51 (C-6); 46.18 (N-CH_3). Anal. calcd. for $C_{10}H_9NO_3$: C, 62.82; H, 4.71; N, 7.32. Found: C, 62.83; H, 4.82; N, 7.06.

5,8-Dihydroxy-1-ethyl-4 (1*H*)-quinolinone **9b**

Starting from compound **6b** (1.03 g, 4.41 mmol), a yield of 904 mg (87%) of **9b** was obtained. Mp, 275 °C. Lit,[11] 270 °C. IR and ^{1}H-NMR, see reference 11. ^{13}C-NMR (63 MHz, d_6-DMSO): 183.37 (C-4); 156.05 (C-5); 149.31 (C-2); 139.48 (C-8); 131.27 (C-8a); 122.49 (C-7); 116.89 (C-4a); 110.33 (C-3); 108.92 (C-6); 54.05 (N-*CH_2* CH_3); 18.77 (N-CH_2*CH_3*).

1-Alkyl-1*H*-4,5,8-quinolinetriones 4

1-Methyl-1*H*- 4,5,8-quinolinetrione **4a**

METHOD A. A suspension of hidroquinone **9a** (275 mg, 1.44 mmol) in acetonitrile (10 ml) was protected from light and cooled to 0 °C. A solution of cerium ammonium nitrate (1.66 g, 2.88 mmol) in cold water (10 ml) was added dropwise. The solution thus obtained was stirred at 0 °C for 20 min and then diluted with water (25 ml) and extracted with chloroform (10 x 50 ml). The combined chloroform layers were dried over sodium sulphate and evaporated under reduced pressure at 25 °C while protected from light. The residue was crystallized from ethyl acetate. Yield, 85 mg (31%).

METHOD B. To a light-protected solution of hidroquinone **9a** (297 mg, 1.55 mmol) in water (40 ml) was added solid activated MnO_2 (947 mg, 10.88 mmol). The suspension was stirred at room temperature for 45 min and extracted with chloroform. The residue from evaporation of the chloroform was purified by rapid chromatography on silica gel, eluting with ethyl acetate. Yield, 120 mg (41 %).

DATA FOR **4a**: Mp, 160 °C. IR (KBr): 1667 and 1624 (C=O) cm^{-1}. ^{1}H-NMR (250 MHz, $CDCl_3$) δ: 7.34 (d, 1H, J = 7.8 Hz, H-2); 6.80 (s, 2H, H-6 and H-7); 6.69 (d, 1H, J = 7.8 Hz, H-3); 3.99 (s, 3H, N-CH_3). ^{13}C-NMR (63 MHz, $CDCl_3$) δ: 183.4, 183.3 and 175.1 (C-4, C-5 and C-8); 144.4 (C-2); 142.4 (C-8a); 138.3 (C-7); 134.7 (C-6); 126 (C-3); 120.2 (C-4a); 41.4 (N-CH_3). Anal. calcd. for $C_{10}H_7NO_3$: C, 63.49; H, 3.70; N, 7.40. Found: C, 63.27; H, 3.87; N, 7.11.

1-Ethyl-1*H*- 4,5,8-quinolinetrione **4b**

The method A described for the synthesis of **4a** was used, starting from 90 mg (0.44 mmol) of compound **7b** and 505 mg (0.92 mmol) of cerium ammonium nitrate. Purification by chromatography on silica gel, eluting with a gradient from ethyl acetate to ethanol, gave 45 mg (51%) of quinone **4b.** Mp, 172 °C. IR (KBr): 1665 and 1620 (C=O) cm^{-1}. ^{1}H-NMR (250 MHz, $CDCl_3$) δ: 7.42 (d, 1H, J = 7.8 Hz, H-2); 6.81 (s, 2H, H-6 and H-7); 6.73 (d, 1H, J = 7.8 Hz, H-3); 4.38 (q, 2H, J = 7 Hz, N-*CH_2* CH_3); 1.49 (t, 3H, J = 7 Hz, N-*CH_2* CH_3). ^{13}C-NMR (63 MHz, $CDCl_3$) δ: 183.40, 183.31 and 175.06 (C-4, C-5 and C-8); 142.77 (C-2); 142.27 (C-8a); 138.26 (C-7); 134.76 (C-6); 126.55 (C-3); 120.55 (C-4a); 52.22 (N-*CH_2* CH_3); 16.04 (N-CH_2*CH_3*). Anal. calcd. for $C_{11}H_9NO_3$: C, 65.05; H, 4.43; N, 6.89. Found: C, 65.27; H, 4.57; N, 6.91.

3-Ethoxycarbonyl-1-methyl-1*H*-4,5,8-quinolinetrione **4c**

To a solution of compound **6c** (323 mg, 1.0 mmol) in chloroform (10 ml), protected from light and cooled to 0 °C, was added a solution of cerium ammonium nitrate (1.15 g, 2 mmol) in cold water (5 ml). The biphasic system was vigorously stirred for 10 min at room temperature and was then diluted with water (15 ml) and

extracted with chloroform (3 x 50 ml). The combined organic layers were dried (sodium sulphate) and evaporated, and the residue was purified by chromatography on silica gel, eluting with ethyl acetate-ethanol (9:1). Yield, 222 mg (85 %). Mp, 162 °C. IR (KBr): 1727 ($COOC_2H_5$); 1663 and 1620 (C=O) cm^{-1}. ^{1}H-NMR (250 MHz, $CDCl_3$) δ: 8.11 (s, 1H, H-2); 6.79 (s, 2H, H-6 and H-7); 4.32 (q, 2H, *J* = 7.1 Hz, $COOCH_2$ CH_3); 4.03 (s, 3H, N-CH_3); 1.34 (t, 3H,*J* = 7.1 Hz, $COOCH_2CH_3$). ^{13}C-NMR (63 MHz, $CDCl_3$): 183.11, 182.80 and 171.27 (C-4, C-5 and C-8); 163.77 (COOEt); 149.44 (C-2); 141.86 (C-8a); 138.29 (C-7); 134.59 (C-6); 125.14 (C-3); 122.68 (C-4a); 61.68 ($COOCH_2$ CH_3); 46.26(N-CH_3); 14.09 ($COOCH_2CH_3$). Anal. calcd. for $C_{13}H_{11}NO_5$: C, 59.80; H, 4.25; N, 5.36. Found: C, 59.73; H, 4.33; N, 5.23.

Hetero Diels-Alder Reactions of Quinones 4. General Procedure.

To a cooled (0 °C) solution of the suitable quinone (*ca.* 0.30 mmol) in dry THF (2 ml), under an argon atmosphere and protected from light, was added over 10 min a solution of the suitable azadiene (2 eq.) in dry THF (10 ml). The solution thus obtained was stirred at room temperature for 1-2 h (reactions of diene **3b**) or for 17 h (reactions of diene **3a**), evaporated and purified by column chromatography on silica gel, eluting with the solvent system indicated in each case.

Reaction between 3a and 4a.

Yield, 33 % of compound **12a** and 30 % of hydroquinone **9a**, after chromatography eluting with a gradient from neat ethyl acetate to neat ethanol.

1,5-Dimethyl-1,8-diazaantracene-4,5,8-trione **12a.** Mp, 198 °C. IR (KBr): 1675, 1629 (CO) cm^{-1}. ^{1}H-NMR (250 MHz, $CDCl_3$) δ: 8.78 (d, 1H, *J* = 4.8 Hz, H-7); 7.49 (d, 1H, *J* = 4.8 Hz, H-6); 7.35 (d, 1H, *J* = 7.8 Hz, H-2); 6.73 (d, 1H, *J* = 7.8 Hz, H-3); 4.06 (s, 3H, N-CH_3); 2.84 (s, 3H, CH_3). ^{13}C-NMR (63 MHz, $CDCl_3$) δ: 182.66, 182.44 and 175.42 (C-4, C-9, C-10); 153 (C-7); 150.78 (C-5); 148.14 (C-8a); 143.98 (C-2); 143.60 (C-9a); 132.15 (C-6); 128.89 (C-10a); 125.88 (C-3); 123.12 (C-4a); 45.73 (N-CH_3); 21.97 (CH_3). Anal. calcd. for $C_{14}H_{10}N_2O_3$: C, 71.82; H, 4.27; N, 11.96. Found: C, 71.92; H, 4.83; N, 11.80.

Reaction between 3a and 4b.

Yield, 26 % of compound **12b** and 23 % of hydroquinone **9b**, after chromatography eluting with a gradient from neat ethyl acetate to neat ethanol.

1-Ethyl-5-methyl-1,8-diazaantracene-4,5,8-trione **12b**. Mp, 210 °C. IR (KBr): 1680,1628 (CO) cm^{-1}. ^{1}H-NMR (250 MHz, $CDCl_3$) δ: 8.77 (d, 1H, *J* = 4.8 Hz, H-7); 7.47 (d, 1H, *J* = 4.8 Hz, H-6); 7.35 (d, 1H, *J* = 7.8 Hz, H-2); 6.75 (d, 1H, *J* = 7.8 Hz, H-3); 4.37 (q, 2H, N-CH_2 CH_3); 2.82 (s, 3H, CH_3); 1.55 (t, 3H, *J* = 7 Hz, N-CH_2CH_3). Anal. calcd. for $C_{15}H_{12}N_2O_3$: C, 67.19; H, 4.47; N, 10.44. Found: C, 66.76; H, 4.88; N, 10.01.

Reaction between 3b and 4a.

Yield, 29 % of hydroquinone **9a**, 33 % of compound **12c** and 3 % of its regioisomer **16a**, after chromatography eluting with a gradient from dichloromethane-ethyl acetate (1:9) to ethyl acetate, then to ethyl acetate-ethanol mixtures and finally to neat ethanol.

1,6-Dimethyl-1,8-diazaantracene-4,5,8-trione **12c**. Mp, 202 °C. IR (KBr): 1697, 1670 and 1626 (C=O) cm^{-1}. ^{1}H-NMR (250 MHz, $CDCl_3$) δ: 8.82 (d, 1H, *J* = 1.2 Hz, H-7); 8.27 (d, 1H, *J* = 1.2 Hz, H-5); 7.44 (d, 1H, *J* = 7.8 Hz, H-2); 6.75 (d, 1H, *J* = 7.8 Hz, H-3); 4.14 (s, 3H, N-CH_3); 2.56 (s, 3H, CH_3). ^{13}C-NMR (63 MHz, $CDCl_3$): 180.78, 180.42 and 175.43 (C-4, C-9 and C-10); 155.26 (C-7); 144.56 (C-9a); 144.55 (C-8a); 144.18 (C-6); 140.37 (C-2); 134.46 (C-5); 129.09 (C-10a); 125.97 (C-3); 121.64 (C-4a); 46.26 (N-CH_3);

19.05 (CH_3). Anal. calcd. for $C_{14}H_{10}N_2O_3$: C, 71.82; H, 4.27; N, 11.96. Found: C, 71.61; H, 4.57; N, 11.81.

1,7-Dimethyl-1,5-diazaantracene-4,5,8-trione **16a**. ^{1}H-NMR (250 MHz, $CDCl_3$) δ: 8.92 (d, 1H, H-6); 8.16 (d, 1H, H-8); 7.30 (d, 1H, *J* = 7.8 Hz, H-2); 6.67 (d, 1H, *J* = 7.8 Hz, H-3); 4.08 (s, 3H, N-CH_3); 2.54 (s, 3H, CH_3).

Reaction between 3b and 4b.

Yield, 56 % of hydroquinone **17a**, 16 % of quinone **12d** and 7.5 % of its regioisomer **16b**, after chromatography eluting with a gradient starting from dichloromethane-ethyl acetate (3:7) to ethyl acetate, then to ethanol-ethyl acetate (3:7) and finally to neat ethanol.

1-Ethyl-6-methyl-9,10-dihydroxy-1,8-diazaanthracen-4(1*H*)-one **17a**. Mp, 172 °C. IR (KBr): 3414 (OH); 1635 (C=O) cm^{-1}. ^{1}H-NMR (250 MHz, $CDCl_3$) δ: 8.64 (d, 1H, *J* = 2 Hz, H-7); 8.41 (d, 1H, *J* = 2 Hz, H-5); 7.42 (d, 1H, *J* = 7.5 Hz, H-2); 5.98 (d, 1H, *J* = 7.5 Hz, H-3); 4.58 (q, 2H, *J* = 7 Hz, N-*CH*$_2$ CH_3); 2.50 (s, 3H, CH_3); 1.47 (t, 3H, *J* = 7 Hz, N-CH_2*CH*$_3$). ^{13}C-NMR (63 MHz, $CDCl_3$): 184.27 (C-4); 153.55 (C-7); 152.85 (C10); 147.36 (C-2); 136.89 (C-6); 131.50 (C-5); 130.64 (C-6); 129.16 (C-9a); 122.50 (C-8a); 117.80 (C-4a); 114.37 (C-10a); 105.01 (C-3); 53.12 (N-*CH*$_2$ CH_3); 18.88 (CH_3); 17.07 (N-CH_2*CH*$_3$).Anal. calcd. for $C_{15}H_{14}N_2O_3$: C, 66.69; H, 5.18; N, 10.36. Found: C, 66.04; H, 5.76; N, 9.85.

1-Ethyl-6-methyl-1,8-diazaantracene-4,5,8-trione **12d**. Mp, 177 °C. IR (KBr): 1694, 1665 and 1625 (C=O) cm^{-1}. ^{1}H-NMR (250 MHz, $CDCl_3$) δ: 8.82 (d, 1H, *J* = 1.5 Hz, H-7); 8.28 (d, 1H, *J* = 1.5 Hz, H-5); 7.46 (d, 1H, *J* = 7 Hz, H-2); 6.79 (d, 1H, *J* = 7 Hz, H-3); 4.45 (q, 2H, *J* = 7 Hz, N-*CH*$_2$ CH_3); 2.56 (s, 3H, CH_3); 1.60 (t, 3H, *J* = 7 Hz, N-CH_2*CH*$_3$) . ^{13}C-NMR (63 MHz, $CDCl_3$): 180.71, 180.53 and 175.42 (C-4, C-9 and C-10); 155.26 (C-7); 144.75 (C-9a); 144.68 (C-8a); 142.81 (C-2); 140.29 (C-6); 134.44 (C-5); 129.05 (C-10a); 126.38 (C-3); 121.84 (C-4a); 52.88 (N-*CH*$_2$ CH_3); 19.04 (CH_3); 16.19 (N-CH_2*CH*$_3$).Anal. calcd. for $C_{15}H_{12}N_2O_3$: C, 67.19; H, 4.47; N, 10.44. Found: C, 67.48; H, 4.55; N, 10.18.

1-Ethyl-7-methyl-1,5-diazaantracene-4,5,8-trione **16b**. Mp, 270-275 °C. IR (KBr): 1676 and 1629 (C=O) cm^{-1}. ^{1}H-NMR (250 MHz, $CDCl_3$) δ: 8.90 (s, 1H, H-6); 8.15 (s, 1H, H-8); 7.36 (d, 1H, *J* = 7.8 Hz, H-2); 6.73 (d, 1H, *J* = 7.8 Hz, H-3); 4.41 (q, 2H, *J* = 7 Hz, N-*CH*$_2$ CH_3); 2.52 (s, 3H, CH_3); 1.55 (t, 3H, *J* = 7 Hz, N-CH_2*CH*$_3$) . ^{13}C-NMR (63 MHz, $CDCl_3$): 182.39, 179.49 and 175.55 (3 C=O); 157.06 (C-6); 145.34 and 143.93 (C-9a and C-10a); 142.88 (C-2); 138.26 (C-7); 134.35 (C-8); 129.11 (C-8a); 126.43 (C-3); 122.86 (C-4a); 52.83 (N-*C*H_2-CH_3); 18.91 (C_7-CH_3); 16.36 (N-CH_2-*C*H_3) ppm. Anal. calcd. for $C_{15}H_{12}N_2O_3$: C, 67.19; H, 4.47; N, 10.44. Found: C, 67.08; H, 4.85; N, 10.78.

Reaction between 3b and 4c.

Yield, 44 % of hydroquinone **17b**, 7 % of quinone **12e** and 4 % of its regioisomer **16c**, after chromatography eluting with ethyl acetate to purify compound **17b** followed by elution with a mixture of ethyl acetate-acetone-ethanol (2:1:1) to give an inseparable mixture of **12e** and **16c**.

Ethyl 1,6-dimethyl-9,10-dihydroxy-4-oxo-1,4-dihydro-1,8-diazaanthracene-3-carboxylate **17b**. Mp, 269 °C. IR (KBr): 3284 (OH); 1679 and 1630 (C=O) cm^{-1}. ^{1}H-NMR (250 MHz, $CDCl_3$) δ: 15.75 (s, 1H, -OH); 8.74 (s, 1H, H-7); 8.52 (s, 1H, H-5); 8.35 (s, 1H, H-2); 4.39 (q, 2H, *J* = 7 Hz, COO*CH*$_2$ CH_3); 4.33 (s, 3H, N-CH_3); 2.56 (s, 3H, CH_3); 1.41 (t, 3H, *J* = 7 Hz, $COOCH_2$ *C*H_3).

3-Ethoxycarbonyl-1,6-methyl-1,8-diazantracene-4,5,8-trione **12e**. Mp, 181 °C. IR (KBr): 1720 ($COOC_2H_5$), 1691 and 1624 (C=O) cm^{-1}. ^{1}H-NMR (250 MHz, $CDCl_3$) δ: 8.78 (d, 1H, *J* = 2 Hz, H-7); 8.22 (d, 1H, *J* = 2.0 Hz, H-5); 8.13 (s, 1H, H-2); 4.31 (q, 2H, *J* = 7.1 Hz, COO*CH*$_2$ CH_3); 4.11 (s, 3H, N-CH_3);

2.49 (s, 3H, CH_3); 1.32 (t, 3H, J = 7.1 Hz, $COOCH_2CH_3$). ^{13}C-NMR (63 MHz, $CDCl_3$): 180.56, 180.28 and 171.75 (C-4, C-5 and C-8); 163.97 ($COOC_2H_5$); 155.66 (C-7); 149.77 (C-2); 144.62 (C-9a); 144.24 (C-8a); 140.63 (C-6); 134.75 (C-5); 129.29 (C-10a); 125.33 (C-3); 124.39 (C-4a); 61.93 ($COOCH_2CH_3$); 46.92 (N-CH_3); 14.33 ($COOCH_2CH_3$). Anal. calcd. for $C_{16}H_{14}N_2O_5$: C, 61.17; H, 4.45; N, 8.91. Found: C, 61.61; H, 4.57; N, 9.61.

3-Ethoxycarbonyl-1,7-dimethyl-1,5 -diazantracene-4,5,8-trione **16c**. ^{1}H-NMR (250 MHz, $CDCl_3$) δ: 8.82 (s, 1H, H-6); 8.27 (s, 1H, H-8); 8.16 (s, 1H, H-2); 4.34 (q, 2H, J = 7.1 Hz, $COOCH_2CH_3$); 4.15 (s, 3H, N-CH_3); 2.53 (s, 3H, CH_3); 1.36 (t, 3H, J = 7.1 Hz, $COOCH_2CH_3$).

Oxidation of 17a,b to 12d,e.

To a solution of the suitable hydroquinone **17** (0.10 to 0.16 mmol) in chloroform (10 ml) was added activated manganese dioxide (1.1 to 2.5 mmol). The black suspension was stirred at room temperature for 1 min and was filtered through a plug of silica gel, eluting with ethyl acetate-methanol (9:1). Evaporation of the solvent afforded compounds **12** in 100 % yield in both cases.

(±) 2-Dimethylhydrazonomethyl-5-hydroxy-2,6-dimethyl-2,3,6,9-tetrahydrofuro[2,3-*f*]-quinolin-9-one 24.

To solution of hydroquinone **7a** (35 mg, 0.18 mmol) in acetonitrile (5 ml), protected from light and cooled to 0 °C, was added a solution of cerium ammonium nitrate (203 mg, 0.37 mmol) in water (2 ml). The reaction mixture was stirred at room temperature for 20 min and was then treated with azadiene **3b** (203 mg, 0.37 mmol). After stirring for 1 min, the solution was diluted with water (10 ml) and extracted with chloroform (3 x 50 ml). The combined chloroform layers were evaporated and the residue was purified by chromatography on silica gel, eluting with ethyl acetate, yielding 41 mg (74 %) of compound **24**. Mp, 119 °C. IR (KBr): 1640 (C=O) cm^{-1}. ^{1}H-NMR (250 MHz, $CDCl_3$) δ: 14.26 (s, 1H, -OH); 7.22 (d, 1H, J = 7.6 Hz, H-7); 6.56 (s, 1H, H-4); 5.99 (d, 1H, J = 7.6 Hz, H-8); 3.99 (s, 3H, N-CH_3); 3.62 (d, 2H, J = 16.3 Hz, H-2); 2.96 (d, 2H, J = 16.3 Hz, CH_3); 2.74 (s, 6H, N-$(CH_3)_2$). ^{13}C-NMR (63 MHz, $CDCl_3$): 182.18 (C-9); 156.00 (C-9b); 145.16 (C-7); 137.86 (C-5); 135.13 (CH=N); 133.24 (C-5a); 127.24 (C-3a); 113.72 (C-9a); 107.74 (C-4); 106.39 (C-8); 88.54 (C-2); 45.00 (N-CH_3); 42.68 (N-$(CH_3)_2$); 40.72 (C-3); 25.41 (CH_3). Anal. calcd. for $C_{16}H_{19}N_3O_3$: C, 63.81; H, 6.31; N, 13.94. Found: C, 63.75; H, 6.01; N, 14.11.

ACKNOWLEDGEMENTS

Financial support from CICYT (grants FAR-553-90 and PTR-0028-93) and Ministerio de Educación y Ciencia (studentship to MMB) is gratefully acknowledged.

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(*Received in UK* 27 *May* 1997; *revised* 13 *June* 1997; *accepted* 19 *June* 1997)