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Cycloaddition of a Furan Analogue of *o*-Quinodimethane with Quinones and their Bromo Derivatives

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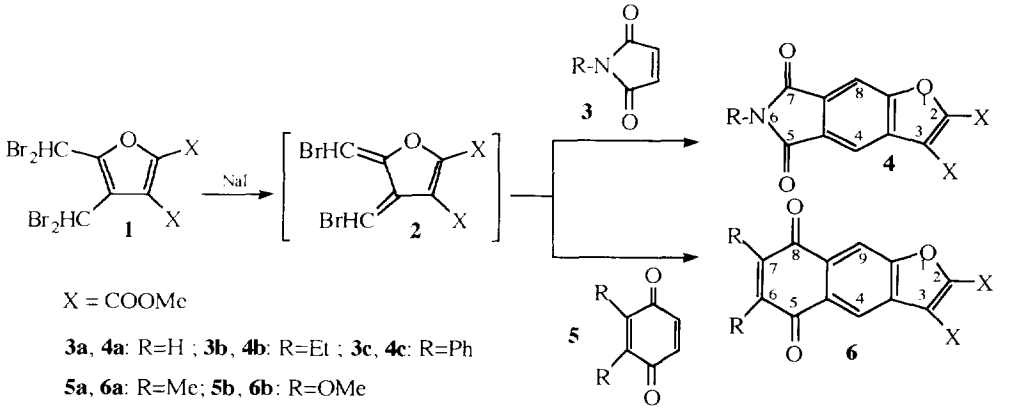
Abstract : Dimethyl-4,5-bis(bromomethylene)furan-2,3-dioate **2**, generated "in situ" from the tetrabromo compound **1** and sodium iodide, was condensed with unsymmetrical quinones **7c-e** , **10** and the 2- or 3-bromo naphthoquinones **8** or **9**. Starting from the latter, the cycloadditions were found more regioselective than from the non brominated quinones. Assignment of the regioisomers was made by 2D ^{1}H-^{13}C HMQC and HMBC techniques performed on **12d**, **11e** and **12e**. Calculations of HOMO and LUMO energies and the orbital coefficients by the semiempirical AM1 method indicate that **2** can be characterized as a rather neutral non polarized diene.

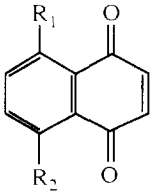
The usefulness of *o*-quinodimethane derivatives in the Diels-Alder synthesis of polycyclic aromatic compounds has been well established.[1] Investigations in the field of their heterocyclic analogues received a recent attention.[2] In a previous communication, we reported the "in situ" generation of dimethyl-4,5-bis (bromomethylene)furan-2,3-dioate **2** in the presence of sodium iodide. [4+2] Cycloadditions of **2** towards symmetrical dienophiles such as maleimides **3** and benzoquinones **5** yielded the aromatized compounds **4** and **6**.[3] (Scheme 1).

Scheme 1

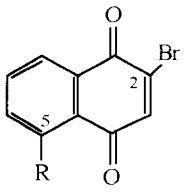


In order to obtain some tetracyclic furoquinones of biological interest, we used naphthoquinone and naphthazarine as dienophiles. Thus, **7a** and **7b** gave similarly in the presence of **2** the aromatized adducts **11a** and **11b** (Scheme 2 and Table 1). We describe, in this paper, condensations of this furan *o*-quinodimethane **2** with the unsymmetrical quinones **7**, **8**, **9** and **10** and then, discuss the regiochemistry of the cycloadditions.

Scheme 2



7



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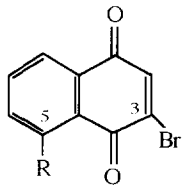

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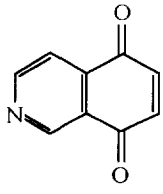
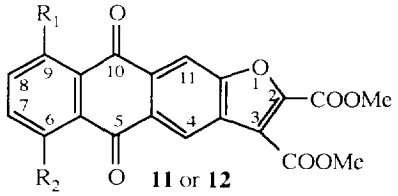


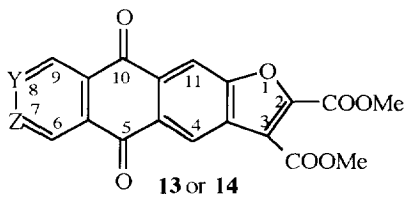
10

7a: R_1= R_2= H
7b: R_1=R_2=OH
7c: R_1=H, R_2=OH
7d: R_1=H, R_2=OAc
7e: R_1=H, R_2=OMe

8c, **9c**: R=OH
8d, **9d**: R=OAc
8e, **9e**: R=OMe



11 or **12**



13 or **14**

11a: R_1= R_2= H
11b: R_1=R_2=OH
11c: R_1=H, R_2=OH
11d: R_1=H, R_2=OAc
11e: R_1=H, R_2=OMe

12c: R_1=OH, R_2=H
12d: R_1=OAc, R_2=H
12e: R_1=OMe, R_2=H

13: Y=CH, Z=N
14: Y=N, Z=CH

RESULTS AND DISCUSSION

Starting from the 5-substituted naphthoquinones **7c-e**, a mixture of the regioisomeric anthra[2,3-*b*]furan-5,10-diones **11** and **12** was obtained (Table 1). The cycloadditions were more regioselective with methyljuglone **7e** than with juglone **7c** or its acetyl derivative **7d** (entries 3-5). The poor regioselectivity observed with **7c** and the wrong 1,6- regioisomers (**12d** and **12e**) obtained as the major products from **7d** and **7e** respectively, are in contrast with high regioselectivities generally induced by the presence of the activating peri-OH substituent and the known directing opposite effect of the donors groups (OAc, OMe) in the corresponding naphthoquinones.[4]

In order to obtain a better regioselectivity, we turned our attention to the use of bromoquinones **8** and **9** for which it was previously reported that the electron rich end of azadienes adds exclusively at the unsubstituted carbon atom of these dienophiles.[5,6] The reactivity of the latter towards *o*-quinodimethane **2** was found

comparable to that of juglone **7c** or its derivatives **7d**, **7e**. Concerning the regiochemistry observed, the cycloadditions were more regioselective with the bromoquinones. Thus, with 2-bromonaphthoquinones **8**, the 1,6- regioisomers **11** were obtained as the major products (entries 6-8) while the 1,9- ones **12** were formed in higher amounts from **9** (entries 9-11). Lastly, the Diels-Alder reaction of **2** and isoquinoline-5,8-dione **10** gave a mixture of the regioisomers 1,7- and 1,8- (entry 12).

Table 1. Cycloadditions of the furan *o*-quinodimethane **2** with quinones **7-10**.

Entry	Starting quinone	NaI (eq.)	Conditions	Compounds	Yield [%]	Ratio of **11** / **12** (1,6- / 1,9-)
1	**7a**	5	3h, 70°C	**11a**	64	
2	**7b**	5	2 h, 60°C	**11b**	72	
3	**7c**	5	2.5 h, 55°C	**11c** + **12c**	80	44 / 56
4	**7d**	5	2.5 h, 55°C	**11d** + **12d**	60	38 / 62
5	**7e**	5	2.5 h, 55°C	**11e** + **12e**	60	23 / 77
6	**8c**	6	2.5 h, 55°C	**11c** + **12c**	72	80 / 20
7	**8d**	6	2.5 h, 55°C	**11d** + **12d**	72	75 / 25
8	**8e**	6	2.5 h, 55°C	**11e** + **12e**	58	73 / 27
9	**9c**	6	2.5 h, 55°C	**11c** + **12c**	82	12 / 88
10	**9d**	6	2.5 h, 55°C	**11d** + **12d**	59	16 / 84
11	**9e**	6	2.5 h, 55°C	**11e** + **12e**	76	12 / 88
12	**10**	5	1h, 60°C	**13**+ **14**	60	46 and 54

The regioisomers **11** and **12** are differentiated by the ^{1}H NMR chemical shifts of H-4 and H-11 (Table 2).

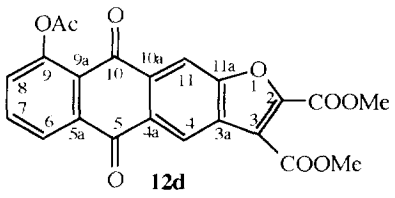
Table 2. ^{1}H NMR chemical shifts (300 MHz, $CDCl_3$, δ ppm) of H-4 and H-11 for compounds **11** and **12**

1,6- Regioisomer	H-4	H-11	1,9- Regioisomer	H-4	H-11
11c	8.97	8.51	**12c**	8.93	8.53
11d	8.85	8.46	**12d**	8.89	8.42
11e	8.89	8.42	**12e**	8.86	8.49

Assignment of the structure for the regioisomers 1,6- and 1,9- was made by 2D ^{1}H-^{13}C NMR HMQC and HMBC correlations performed on samples containing more than 95 % of **12d**, **11e** and **12e** respectively. These techniques permit to correlate the protons with the carbon atoms through the ^{1}J, ^{2}J, ^{3}J and ^{4}J ^{1}H-^{13}C couplings. ^{1}J Couplings were confirmed by the HMQC method while long range couplings were identified by HMBC correlations for which ^{3}J values are larger than ^{2}J or ^{4}J in aromatic compounds. As an example, we report in Table 3 these spectral data for **12d**. Thus, the two ^{3}J couplings of C-5 with H-4 and H-6, on one hand, and the ^{3}J coupling between C-3 and H-4, on the other hand, allow to assign the position of the acetoxyl

group at C-9. In the hypothesis of an opposite 1,6- regioisomer, C-5 would present a ^3J correlation only with H-4 while C-10 would have a second one with H-9. Then, compound **11d** was assigned as a 1,6- regioisomer. Furthermore, these NMR correlations applied to **11e** and **12e** agree with 1,6- and 1,9- structures respectively.

Table 3. 2D ^1H-^{13}C NMR HMQC and HMBC correlations for compound **12d** ($CDCl_3$, δ ppm)



12d

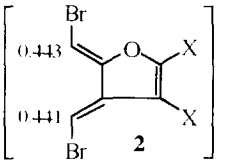
Position	^1H (300 MHz)	^{13}C (75 MHz)	HMQC ^1J	HMBC (C-H couplings)			
				^1J	^2J	^3J	^4J
2	-	149.8	-	-	-	-	-
3	-	118	-	-	-	H-4	-
3a	-	129.78	-	-	-	H-11	-
4	8.89	123.7	H-4	H-4	-	-	H-11
4a	-	129.77	-	-	-	H-11	-
5	-	181.3	-	-	-	H-4	H-11
						H-6	
5a	-	135.2	-	-	-	H-7	-
6	8.34	126	H-6	H-6	H-7	H-8	-
7	7.83	135.1	H-7	H-7	-	-	-
8	7.45	130	H-8	H-8	H-7	H-6	-
9	-	150.3	-	-	H-8	H-7	-
9a	-	125.1	-	-	H-8	H-6	H-7
10	-	180.6	-	-	-	H-11	H-4
10a	-	133.8	-	-	-	H-4	H-11
11	8.42	111.5	H-11	H-11	-	-	H-4
11a	-	156.3	-	-	H-11	H-4	-

Treatment of the acetate **12d** with 10 % KOH in ethanol gave the corresponding hydroxylated derivative. The ^1H-NMR spectrum of this compound is identical with that of **12e**. Therefore, **11e** and **12e** are assigned to be 1,6- and 1,9- regioisomers. A poor regioselectivity was also observed in the cycloaddition of **2** with isoquinoline-5,8-dione. In this case, the regioisomeric 1,7- and 1,8- structures are not demonstrated.

In order to better characterize the behavior of *o*-quinodimethane **2** in cycloaddition reactions, we calculated HOMO and LUMO energies by the semiempirical AM1 method[7] for the more stable (E, Z) configuration (Table 4). Comparison of the HOMO and LUMO values of **2** (-9.317 and -1.662 respectively)

with those of buta-1,3-diene (HOMO = -9.335 and LUMO = 0.464) and 1-methoxybuta-1,3-diene (HOMO = -8.716 and LUMO = 0.499) indicate that **2** can be rather considered as an electron neutral diene. Calculations of the orbital coefficients at the ends of **2** suggest that its reactions with unsymmetrical and polarized dienophiles should not be higly regioselective. Calculations by the same method of the orbital coefficients for bromonaphthoquinones **8** and **9** show that the larger values are located on the unsubstituted carbon atoms C-3 and C-2 respectively of the corresponding quinones with an exception for **9e** (Table 4). Lastly, the regiochemistry observed in the cycloadditions of **2** and **8** or **9** agrees with that predicted from the orbital coefficient values.

Table 4. Orbital coefficients of *o*-quinodimethane **2** and unsymmetrical naphthoquinones **7**, **8**, **9**

Compound	Formula		
2	 **2**	–	–
	Naphthoquinone	C-2	C-3
7c	5-hydroxy- (syn)	0.341 (0.35)*	0.331 (0.32)*
7d	5-acetoxy-	0.326	0.335
7e	5-methoxy-	0.32 (0.31)*	0.33 (0.33)*
8c	2-bromo-5-hydroxy-	0.334	0.368
8d	2-bromo-5-acetoxy-	0.335	0.351
8e	2-bromo-5-methoxy-	0.340	0.358
9c	3-bromo-5-hydroxy	0.377	0.357
9d	3-bromo-5-acetoxy	0.381	0.350
9e	3-bromo-5-methoxy	0.353	0.356

*Values in the brackets were previously calculated by the SFC STO-3G method.[8]

CONCLUSION

This work describes useful [4+2] cycloadditions of a furan *o*-quinodimethane (**2**) generated "in situ" with unsymmetrical quinones to afford anthrafuran-5,10-diones. The use of 2- or 3-bromonaphthoquinones ameliorates the regioselectivity of the reactions. The structures of the corresponding 1,6- and 1,9-regioisomers are assigned by high resolution NMR techniques. Semiempirical calculations explain the weak regiochemistry or the lack of regiospecificity observed with **2** and quinones **7** or **8** and **9**.

EXPERIMENTAL SECTION

IR spectra were obtained on a Perkin-Elmer 1310 spectrophotometer. Elemental analyses were performed at the Service Central de Microanalyse du CNRS (Solaize, France). Melting points were determined with a Kofler apparatus. Thin-layer chromatographic analyses (TLC) were performed on silica gel 60 F_{254} on aluminum sheets (Merck). Column chromatography is carried out with Matrex Amicon (60 Å, 35-70 μm) silica gel.

^1H and ^{13}C-NMR spectra were recorded on a Bruker AM 300 with tetramethylsilane as an internal standard. For carrying out 2D ^1H-^{13}C HMBC spectra, 5 mg of compounds **12d**, **11e** or **12e** were dissolved at room temperature in 0.5 ml of $CDCl_3$. The HMBC and HMQC techniques were performed with gradients selection [9] which give very clean 2D matrix without any T_1 noise. The J filter and the transfer time for long range coupling were fixed respectively to 3.12 ms and 60 ms. The acquisition parameters were : AQ = 0.622 s, SW2 = 822 Hz, SW1 = 5554 ,NE = 512, NS = 32 Hz, relaxation delay D_1 = 1,4 s. Prior to the FFT, the signal was weighted by a none shifted sinbell in the two dimensions. The size of the final matrix was 1k.1k.

The energies and coefficients of the molecular frontier orbitals were calculated from MOPAC of SYBYL program on an IBM Risk 6000 workstation.

The preparation of dimethyl-4,5-bis(dibromomethyl)furan-2,3-dioate **1** was previously described.[3] 2-Bromo-5-hydroxynaphthoquinone **7c** and 2-bromo-5-acetoxynaphthoquinone **7d** were prepared according to Grunwell et al.[10] 3-Bromo-5-hydroxynaphthoquinone **8c** was obtained by treating juglone with bromine in glacial acetic acid.[11] By this method 13 % of the 2-bromo derivative **7c** was also formed which was eliminated by recrystallization from acetone. Acetylation and methylation of **7c** and **8c** was performed as described for **6d** and **6e**.[12] The melting points of **7** and **8** are identical with the values reported in the literature.[13,14]

6-Ethyl-2,3-dimethoxycarbonyl furo[2,3-*f*]isoindol-6*H*-5,7-dione 4b

m.p. 103°C (AcOEt); yield : 35 % ; IR (KBr) ν 1775 (CO), 1740 (CO), 1710 (CO) cm^{-1}; ^1H-NMR ($CDCl_3$, 300 MHz) δ ppm 8.48 (s, 1H, H-4), 8.02 (s, 1H, H-8), 4.06 (s, 6H, 2 $COOCH_3$), 3.80 (q, 2H, J=7.2 Hz, $\underline{CH_2}CH_3$), 1.31 (t, 3H, J=7.2 Hz, $CH_2\underline{CH_3}$). Anal. Calcd for $C_{16}H_{13}NO_7$, 0.1 H_2O : C, 57.69 ; H, 3.99 ; N, 4.20. Found : C, 57.41 ; H, 3.88 ; N, 4.24.

2,3-Dimethoxycarbonyl-6-phenyl furo[2,3-*f*]isoindol-6*H*-5,7-dione 4c

m.p. 163°C (AcOEt); yield : 58 % ; IR (KBr) 1775 (CO), 1755 (CO), 1720 (CO) cm^{-1}; ^1H-NMR ($CDCl_3$, 300 MHz) δ ppm 8.58 (s, 1H, H-4), 8.13 (s, 1H, H-8), 7.50 (m, 5H, H aromat.), 4.10 (s, 6H, 2 $COOCH_3$). Anal. Calcd for $C_{20}H_{13}NO_7$: C, 63.32 ; H, 3.45 ; N, 3.69. Found : C, 63.28 ; H, 3.63 ; N, 3.90.

6,7-Dimethoxy-2,3-dimethoxycarbonyl naphtho[2,3-*b*]furan-5,8-dione 6b

m.p. 164°C (AcOEt); yield : 62 % ; IR (KBr) ν 1750 (CO), 1725 (CO), 1630 (CO) cm^{-1}; ^1H-NMR ($CDCl_3$, 300 MHz) δ ppm 8.65 (s, 1H, H-4), 8.24 (s, 1H, H-9), 4.15 (s, 3H, OCH_3), 4.14 (s, 3H, OCH_3), 4.05 (s, 3H, $COOCH_3$), 4.04 (s, 3H, $COOCH_3$). Anal. Calcd for $C_{18}H_{14}O_9$, 0.4 H_2O : C, 56.66 ; H, 3.91. Found : C, 56.58 ; H, 3.65.

General procedure for cycloadditions of *o*-quinodimethane 2 with quinones 7, 8, 9 and 10

A solution of the tetrabromo derivative **1** (0.316 g, 0.6 mmol) in DMF (2 ml) was slowly added under stirring to a solution, previously heated at 55°C, of the corresponding quinone (0.5 mmol) and NaI (5 eq. for quinones **7** and **10** or 6 eq. for **8** and **9**) in 3 ml of DMF. Stirring and heating were maintained for a variable time, the evolution of the reaction being followed by TLC. After the usual work-up, the tetracyclic quinones were recrystallized from an appropriate solvent.

2,3-Dimethoxycarbonyl anthra[2,3-*b*]furan-5,10-dione 11a

m.p. 207°C (AcOEt); IR (KBr) ν 1740, 1715, 1680 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ ppm 8.94 (s, 1H, H-4), 8.52 (s, 1H, H-11), 8.37 (m, 2H, H-7 and H-8), 7.85 (m, 2H, H-6 and H-9), 4.09 (s, 3H, $COOCH_3$), 4.08 (s, 3H, $COOCH_3$). Anal. Calcd for $C_{20}H_{12}O_7$: C, 65.93 ; H, 3.32. Found : C, 65.59 ; H, 3.37.

6,9-Dihydroxy-2,3-dimethoxycarbonyl anthra[2,3-*b*]furan-5,10-dione 11b

m.p. 222°C (DMF); IR (KBr) ν 1740, 1715, 1630 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ ppm 12.96 (s, 1H, OH), 12.88 (s, 1H, OH), 8.99 (s, 1H, H-4), 8.56 (s, 1H, H-11), 7.35 (s, 2H, H-7 and H-8), 4.09 (s, 3H, $COOCH_3$), 4.08 (s, 3H, $COOCH_3$). Anal. Calcd for $C_{20}H_{12}O_9$, 0.5 H_2O : C, 59.26 ; H, 3.23. Found : C, 59.05 ; H, 3.00.

2,3-Dimethoxycarbonyl-6 (and 9)-hydroxy anthra[2,3-*b*]furan-5,10-diones 11c and 12c

IR (KBr) ν 1740, 1670, 1640 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ ppm : **11c** (1,6-regioisomer) 12.69 (s, 1H, OH-6), 8.97 (s, 1H, H-4), 8.51 (s, 1H, H-11), 7.91 (d, 1H, J=7.0, H-9), 7.73 (dd, 1H, J=7.0, H-8), 7.35 (d, 1H, J=7.0, H-7), 4.09 (s, 3H, $COOCH_3$), 4.08 (s, 3H, $COOCH_3$); **12c** (1,9-regioisomer) 12.60 (s, 1H, OH-9), 8.93 (s, 1H, H-4), 8.53 (s, 1H, H-11), 7.91 (d, 1H, J=7.0, H-6), 7.73 (dd, 1H, J=7.0, H-7), 7.35 (d, 1H, J=7.0, H-8), 4.09 (s, 3H, $COOCH_3$), 4.08 (s, 3H, $COOCH_3$). Anal. Calcd for $C_{20}H_{12}O_8$, 0.15 H_2O : C, 62.72 ; H, 3.23. Found : C, 62.55 ; H, 2.92.

6 (and 9)-Acetoxy-2,3-dimethoxycarbonyl anthra[2,3-*b*]furan-5,10-diones 11d and 12d

IR (KBr) ν 1760, 1740, 1680 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ ppm : **11d** (1,6-regioisomer) 8.85 (s, 1H, H-4), 8.46 (s, 1H, H-11), 8.33 (d, 1H, J=8.0, H-9), 7.82 (dd, 1H, J=8.0, H-8), 7.44 (d, 1H, J=8.0, H-7), 4.07 (s, 3H, $COO\underline{CH_3}$-2), 4.06 (s, 3H, $COO\underline{CH_3}$-3), 2.52 s, 3H, $OCO\underline{CH_3}$-6). **12d** (1,9-regioisomer) 8.89 (s, 1H, H-4), 8.42 (s, 1H, H-11), 8.34 (d, 1H, J=8.0, H-6), 7.83 (dd, 1H, J=8.0, H-7), 7.45 (d, 1H, J=8.0, H-8), 4.07 (s, 3H, $COO\underline{CH_3}$-2), 4.06 (s, 3H, $COO\underline{CH_3}$-3), 2.52 (s, 3H, $OCO\underline{CH_3}$-9); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ ppm : 181.3 (CO-5), 180.6 (C-10), 169.5 ($O\underline{C}OCH_3$-9), 161.43 ($\underline{C}OOCH_3$-2), 158.3 ($\underline{C}OOCH_3$-3), 156.3 (C-11a), 150.3 (C-9), 149.8 (C-2), 135.2 (C-5a), 135.1 (C-5), 133.8 (C-10a), 130.0 (C-8), 129.78 (C-3a), 129:77 (C-4a), 126.0 (C-6), 125.1 (C-9a), 123.7 (C-4), 118.0 (C-3), 111. 5 (C-11), 53.4 ($COO\underline{CH_3}$-2), 52.92 ($COO\underline{CH_3}$-3), 21.11 ($OCO\underline{CH_3}$-9). Anal. Calcd for $C_{22}H_{14}O_9$, 0.2 H_2O : C, 62.03 ; H, 3.40. Found : C, 61.93 ; H, 3.42.

6 (and 9)-Methoxy-2,3-dimethoxycarbonyl anthra[2,3-*b*]furan-5,10-diones 11e and 12e

IR (KBr) ν 1750, 1730, 1675 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ ppm : **11e** (1,6-regioisomer) 8.89 (s, 1H, H-4), 8.42 (s, 1H, H-11), 8.02 (d, 1H, J=8.0, H-9), 7.76 (dd, 1H, J=8.0, H-8), 7.39 (d, 1H, J=8.0,

H-7), 4.07 (s, 6H, 2 $COOCH_3$), 4.06 (s, 3H, OCH_3-6); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ ppm : 182.69 (C-10), 181.59 (C-5), 161.57 ($COOCH_3$-2), 160.67 (C-6), 158.54 ($COOCH_3$-3), 155.84 (C-11a), 149.76 (C-2), 135.98 (C-9a), 135.2 (C-8), 132.4 (C-10a), 132.21 (C-3a), 130.08 (C-4a), 124.05 (C-4), 121.69 (C-5a), 120.03 (C-9), 118.3 (C-7), 118.28 (C-3), 110.7 (C-11), 56.62 (6-OCH_3), 53,37 ($COOCH_3$-2), 52.83 ($COOCH_3$-3). **12e** (1,9-regioisomer) : 8.86 (s, 1H, H-4), 8.49 (s, 1H, H-11), 8.02 (d, 1H, J=8.0, H-6), 7.72 (dd, 1H, J=8.0, H-7), 7.35 (d, 1H, J=8.0, H-8), 4.07 (s, 6H, 2 $COOCH_3$), 4.06 (s, 3H, OCH_3); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ ppm : 182.46 (C-5), 181.33 (C-10), 161.64 ($COOCH_3$-2), 160.61 (C-9), 158.41 ($COOCH_3$-3), 156.54 (C-11a), 149.45 (C-2), 135.8 (C-5a), 135.4 (C-7), 135.02 (C-10a), 129.7 (C-3a), 129.24 (C-4a), 123.37 (C-4), 121.66 (C-9a), 120.1 (C-6), 118.3 (C-3), 118. 26 (C-8), 111.56 (C-11), 56.6 (OCH_3-6), 53,37 ($COOCH_3$-2), 52.93 ($COOCH_3$-3). Anal. Calcd for $C_{21}H_{14}O_8$, 0.5 H_2O : C, 62.53 ; H, 3.74. Found : C, 62.23 ; H, 3.35.

2,3-Dimethoxycarbonyl-7 (and 8)-azaanthra[2,3-*b*]furan-5,10-diones 13 and 14

m.p. 158°C (AcOEt); IR (KBr) ν 1755, 1735, 1680 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ ppm : **13** + **14** (1,7-and 1,8-regioisomers) 9.64 (s, 1H, H-6 or H-9), 9.62 (s, 1H, H-6 or H-9), 9.15 (d, 2H, J=5.0 Hz, H-7 and H-8), 8.98 (s, 1H, H-4), 8.96 (s, 1H, H-4), 8.54 (s, 1H, H-11), 8.52 (s, 1H, H-11), 8.13 (m, 2H, H-6 and H-9), 4.09 (s, 12H, 4 $COOCH_3$). Anal. Calcd for $C_{19}H_{11}NO_7$, 0.3 H_2O : C, 61.57 ; H, 3.15 ; N, 3.77. Found : C, 61.58 ; H, 3.04 ; N, 3.75.

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