Reaction of 2,5-Dimethylpyrroles with Quinones. Synthesis of New Pyrrolylquinones Dyes

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The reaction of 1,4-naphthoquinone (**1**) with 2,5-dimethylpyrroles (**7a**-**7d**) gives only 3-(1,4-naphthoquinonyl)-2,5-dimethylpyrroles. Extending the reaction to other quinones: 5-hydroxy-1,4-naphthoquinone (**2**), 1,2-naphthoquinone (**3**), quinoline-5,8-dione (**4**) and quinoxaline-5,8-dione (**5**), of which nothing was known, allows the synthesis of new pyrrolylquinones.

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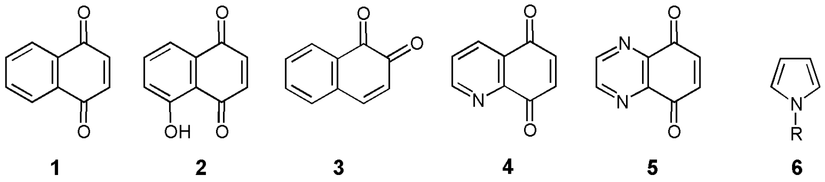
Introduction.

In a previous paper [1a] we reported the synthesis of new organic dyes in the pyrrolylnaphthoquinone family. The structures were obtained by the reaction of 1,4-naphthoquinone (**1**), 5-hydroxy-1,4-naphthoquinone (juglone, **2**), 1,2-naphthoquinone (**3**), quinoline-5,8-dione (**4**) and quinoxaline-5,8-dione (**5**) with *N*-alkylated pyrroles (**6**) [1,2], (Scheme 1).

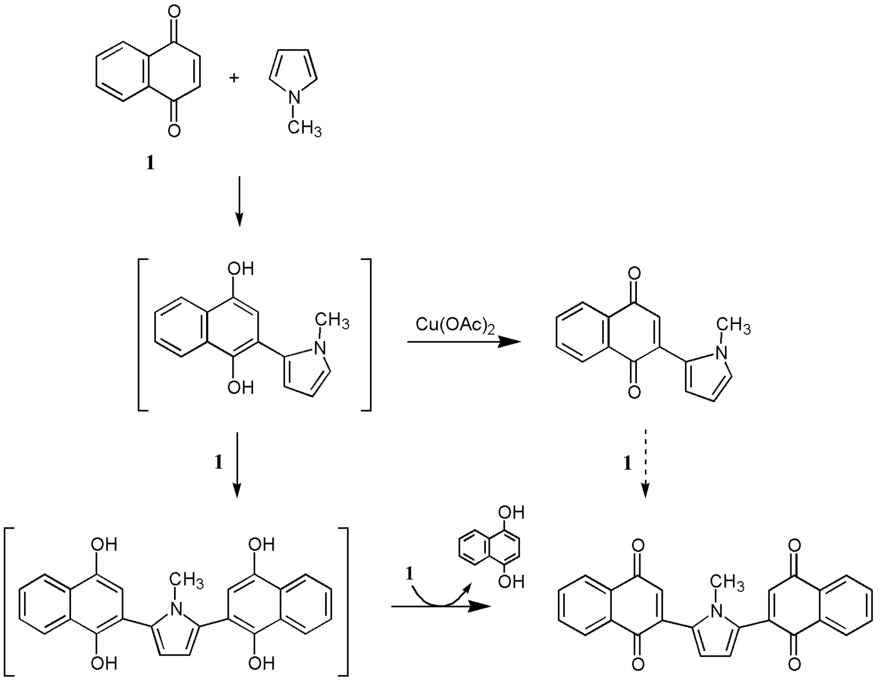
The general pathway for the synthesis of monoquinonyl- or diquinonylpyrroles is given in Scheme 2 [1-3]:

Usually the reaction gives a complex mixture of mono- and di-quinonylpyrroles besides polymers and tars. It is known that the 2 and 5 positions of the pyrroles are the most reactive and give polymers in the presence of metallic salts [1a]. In all cases the pyrroles (**6**) used had free 2 and 5 positions.

Scheme 1



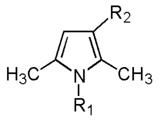
Scheme 2



Our interest in the preparation of new dyes for hair coloration [1b] prompted us to use 2,5-disubstituted pyrroles to avoid secondary products. Very little is known about the reactions of 2,5-disubstituted pyrroles with naphthoquinones. Some previous papers [4-6] reported the reaction of 1,4-benzoquinones with 2,5-dimethylpyrrole leading to disubstituted 3,4-dibenzoquinonyl-2,5-dimethylpyrroles or the substitution reaction of 2,3-dichloronaphthoquinone with 1,2,5-trimethylpyrrole giving 2-chloro-3-[3-(1,2,5-trimethylpyrrolyl)]-1,4-naphthoquinone [7].

We describe here our results on the reaction of quinones (**1**-**5**) with 2,5-disubstituted pyrroles (**7**) (Scheme 3): new organic dyes have been synthesized by this method and tested for application in hair coloration [1b].

Scheme 3



7a $R_1 = R_2 = H$
7b $R_1 = H, R_2 = CO_2CH_3$
7c $R_1 = CH_3, R_2 = H$
7d $R_1 = CH_3, R_2 = CO_2CH_3$

Results-Discussion.

I- Quinone Synthesis.

a- Quinoline-5,8-dione (**4**).

This compound is prepared in three steps from commercial 8-hydroxyquinoline. The nitrosation of 8-hydroxyquinoline followed by reduction leads to 5-amino-8-hydroxyquinoline which by hydrolysis and oxidation affords quinone (**4**) in 29% overall yield [8] (Scheme 4).

b- Quinoxaline-5,8-dione (**5**).

Compound (**5**) is obtained in five steps from commercial 1,4-dimethoxybenzene. The nitration of this product leads to a mixture of 2,5-dinitro- (64%) and 2,3-dinitro-1,4-dimethoxybenzene (16%) [9]. The two isomers are used without separation [10]; catalytic hydrogenation [11] followed by condensation with glyoxal gives pure 5,8-dimethoxyquinoxaline and allows the separation from 2,3-dinitro-1,4-dimethoxybenzene. The hydrogenation step was also performed with tin in HCl [12]. Different methods for demethylation of the dimethoxyquinoline [11,13-15] give quinoxaline-5,8-dione (**5**); best results were obtained by using ceric ammonium nitrate (CAN) [14]. The overall yield of the synthesis is about 13% (Scheme 5).

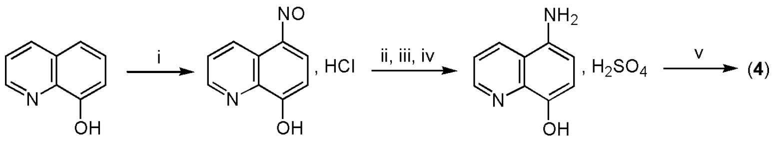
II- Condensation of Pyrroles (**7a**-**7d**) with Quinones.

a- 1,4-Naphthoquinone (**1**) and 5-Hydroxy-1,4-naphthoquinone (**2**).

The best yield is observed using acetic acid, with an excess of naphthoquinone to oxidise the intermediate hydroquinone at room temperature. The reaction is complete in two hours and gives compounds (**8a**-**8d**) besides polymers and tars.

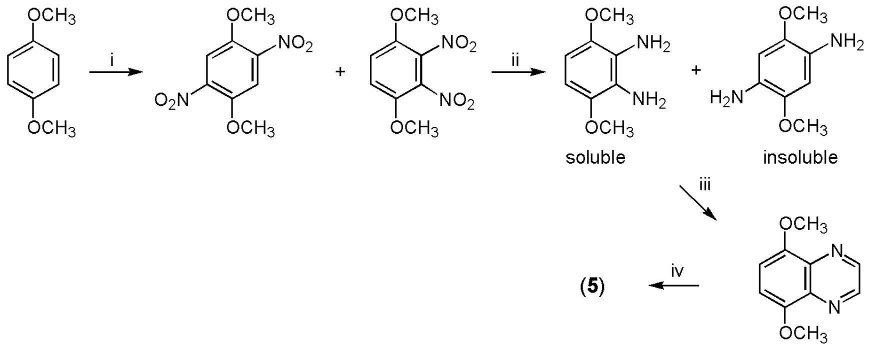
In the case of 5-hydroxy-1,4-naphthoquinone (**2**) under the same conditions, the yields are lower than with 1,4-naphthoquinone (**1**), and the only compound (**9a**-**9d**) obtained has the pyrrole substituent at the 3 position of juglone (**2**). The structures were assigned by nmr studies of long-distance heteronuclear ^{13}C–^{1}H coupling [15]. The nmr ^{13}C spectrum of (**9c**) (Figure) shows the C_1 and C_4

Scheme 4



Reagents: i, $NaNO_2$, HCl; ii, 5*N* NaOH; iii, $Na_2S_2O_4$; iv, 12*N* H_2SO_4; v, $K_2Cr_2O_7$, 12*N* H_2SO_4.

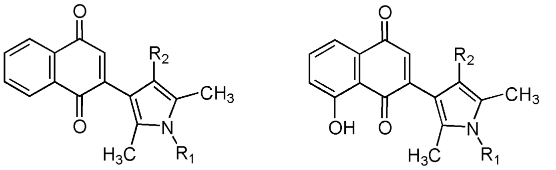
Scheme 5



Reagents: i, HNO_3, AcOH; ii, H_2 (2-3 bars), PtO_2, EtOH; iii, $[CH(OH)SO_3Na]_2$, H_2O; iv, $Ce(NH_4)_2(NO_3)_6$, CH_3CN.

atoms as a singlet (δ: 184.5 ppm) and a doublet (δ: 191.2 ppm, $^3J_{C4\text{-}H2}$= 10.2 Hz), respectively, in accordance of the literature values for pyrrole substitution at the 3 position of juglone [16].

Scheme 6



8a $R_1 = R_2 = H$
8b $R_1 = H$, $R_2 = CO_2CH_3$
8c $R_1 = CH_3$, $R_2 = H$
8d $R_1 = CH_3$, $R_2 = CO_2CH_3$

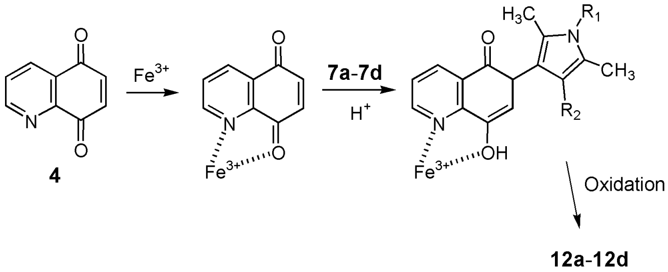
9a $R_1 = R_2 = H$
9b $R_1 = H$, $R_2 = CO_2CH_3$
9c $R_1 = CH_3$, $R_2 = H$
9d $R_1 = CH_3$, $R_2 = CO_2CH_3$

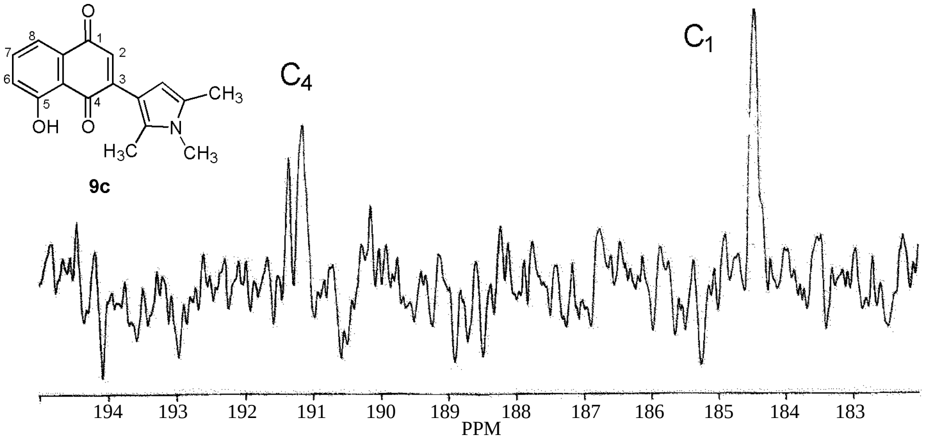
Neither with 1,4-naphthoquinone (**1**) nor with 5-hydroxy-1,4-naphthoquinone (**2**) were disubstituted quinonylpyrroles obtained [1].

c- Quinoline-5,8-dione (**4**) and Quinoxaline-5,8-dione (**5**).

The reaction is performed in a water/chloroform mixture (1:1) with 20% of acetic acid using an excess of pyrrole and $FeCl_3$ as complexing and oxidising agent [2,18]. Under these conditions only compounds with the pyrrolyl at the 6 position of the quinoline-5,8-dione (**4**) are obtained. The reaction is rapid but in the case of 2,5-dimethylpyrrole (**7a**) the condensation product (**12a**) is not isolated; a metallic salt such as $FeCl_3$ is well known to polymerise 2,5-dimethylpyrrole [19] (Table).

Scheme 8



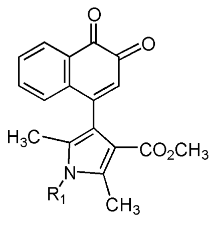


Figure

b- 1,2-Naphthoquinone (**3**).

In acetic acid the reaction of (**3**) with pyrroles (**7**) is fast and gives polymers and tars. In ethyl alcohol with a catalytic amount of *p*-toluenesulfonic acid at room temperature the reaction is slow and leads to 60-70% of the quinonylpyrroles (**10**, **11**) (Table).

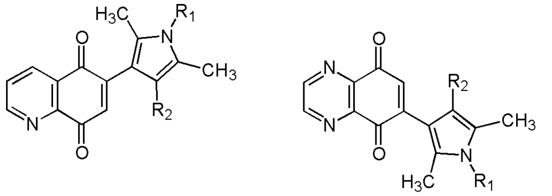
Scheme 7



10 $R_1 = H$
11 $R_1 = CH_3$

The structures (**12a-12d**) were assigned by comparison of the nmr data with literature values [20]. It has also been shown that in the presence of $FeCl_3 \bullet 6H_2O$ (Scheme 8) only the 6-substituted isomers are formed [20].

Scheme 9



12a $R_1 = R_2 = H$
12b $R_1 = H$, $R_2 = CO_2CH_3$
12c $R_1 = CH_3$, $R_2 = H$
12d $R_1 = CH_3$, $R_2 = CO_2CH_3$

13a $R_1 = R_2 = H$
13b $R_1 = H$, $R_2 = CO_2CH_3$
13c $R_1 = CH_3$, $R_2 = H$
13d $R_1 = CH_3$, $R_2 = CO_2CH_3$

In the case of 5,8-quinoxalinedione, the condensation is very slow and 44-61% of product (**13b-13d**) is formed after 48 hours reaction.

Table

Entry	Quinone	Pyrrole	Compound	Yield (%)	Mp (°C)
1	**1**	**7a**	**8a**	56	177-179
2		**7b**	**8b**	39	209-210
3		**7c**	**8c**	42	162-163
4		**7d**	**8d**	51	184-186
5	**2**	**7a**	**9a**	37	195-196
6		**7b**	**9b**	31	182-183
7		**7c**	**9c**	33	181-182
8		**7d**	**9d**	26	172-174
9	**3**	**7b**	**10**	72	176-179
10		**7d**	**11**	65	188-189
11	**4**	**7a**	**12a**	0 [a]	-
12		**7b**	**12b**	19	220-221
13		**7c**	**12c**	59	237-241
14		**7d**	**12d**	22	171-172
15	**5**	**7a**	**13a**	0 [a]	-
16		**7b**	**13b**	44	209-210
17		**7c**	**13c**	56	196-197
18		**7d**	**13d**	61	235-237

[a] Tars, polymers.

In this work we have prepared new 2,5-dimethylpyrrolylquinones from several quinones (**1**-**5**). When the reactive 2 and 5 positions of the pyrrole are substituted, the reaction with quinones occurs in the 3 position. New 2,5-dimethylpyrrolylquinones in the 1,4-naphthoquinone, 1,2-naphthoquinone, quinoline-5,8-dione and quinoxaline-5,8-dione series have been obtained.

EXPERIMENTAL

With the exception of quinones (**4**) and (**5**), all starting materials (**1**, **2**, **3**, **7a**-**7d**) were purchased from Aldrich. Melting points were taken on a Mettler FP 5 capillary apparatus. The ir spectra were recorded on a Perkin-Elmer 781 spectrophotometer. The uv spectra were recorded on a Shimadzu UV/Vis 240 spectrophotometer. The ^{1}H and ^{13}C nmr spectra were run on a Bruker W 200 spectrophotometer at 200 MHz and 50 MHz, respectively, using $CDCl_3$ or DMSO-d_6 as the solvent and are referenced to tetramethylsilane (TMS). The mass spectra were obtained on a Finnigan Mat 800 ITD coupled with a CP - Sil 5 GC column (chemical ionisation using isobutane) or a Nermag R-30-10 (with direct introduction, chemical ionisation using NH_3). All the compounds have one spot by tlc on silica gel 60 F_{254} (Merck). Column chromatography was performed on Matrex LC 60A (silica gel, 35-70 µm, Grace Davidson). Because partially decomposition for these highly conjugated compounds, the elementary microanalysis are still not satisfactory, despite several attempts (only 0.6 – 0.7% instead 0.4%). The high resolution mass spectra were obtained at the Laboratoire de l'Activation Moléculaire of the Ecole Normale Supérieure. Organic solutions, after drying with anhydrous $MgSO_4$, were concentrated at T° < 60 °C under reduced pressure.

General Procedure for the Preparation of Compounds (**8a**-**8d**) and (**9a**-**9d**).

A solution of 1,4-naphthoquinone (**1**) or 5-hydroxy-1,4-naphthoquinone (**2**) (40 mmol) and pyrrole (**7**, 10 mmol) in glacial acetic acid (50 mL) was stirred for two hours at room temperature. The solvent was removed under vacuum and the residue dissolved in chloroform (50 mL) and water (50 mL). Extraction by chloroform (3 X 100 mL), washing the combined organic solutions with a saturated solution of sodium carbonate (30 mL), then with water (50 mL) gave after drying ($MgSO_4$) the crude products. The pyrrolylquinones (**8a-8d** and **9a-9d**) were isolated by column chromatography [SiO_2, $CHCl_3$].

2-(2,5-Dimethyl-1*H*-pyrrol-3-yl)-1,4-naphthoquinone (**8a**).

This compound was obtained as a red solid (56%), mp 177-179 °C; ^{1}H nmr ($CDCl_3$): δ 2.28 (s, 3H), 2.39 (s, 3H), 6.24 (dq, 1H, J = 0.9 Hz, J = 2.9 Hz), 6.84 (s, 1H), 7.68-7.77 (m, 2H), 7.93 (s, 1H), 8.08-8.17 (m, 2H); ms (isobutane) m/z 252 (MH^+); uv (THF) λ_{max} (lg ε) = 248 (4.13), 294 (4.05), 501 (3.40); ir (KBr) ν 3290 cm^{-1} (N-H), 1640, 1665 cm^{-1} (C=O); hrms (FAB) m/z Calcd. for $C_{16}H_{14}NO_2$ (MH^+): 252.1025; Found: 252.1024.

Methyl 4-(1,4-Dioxo-1,4-dihydronaphthalen-2-yl)-2,5-dimethyl-1*H*-pyrrole-3-carboxylate (**8b**).

This compound was obtained as a orange solid (39%), mp 209-210 °C; ^{1}H nmr ($CDCl_3$): δ 2.20 (s, 3H), 2.46 (s, 3H), 3.61 (s, 3H), 6.77 (s, 1H), 7.70-7.78 (m, 2H), 8.06-8.16 (m, 2H), 8.57 (s, 1H); ms (isobutane) m/z 309 (M^+); uv (THF) λ_{max} (lg ε) = 294 (3.68), 245 (4.01), 266 (3.92), 453 (3.10); ir (KBr) ν 3360 cm^{-1} (N-H), 1640, 1665 cm^{-1} (C=O, quinone), 1710 cm^{-1} (C=O, ester); hrms (FAB) m/z Calcd. for $C_{18}H_{16}NO_4$ (MH^+): 310.1079; Found: 310.1073.

2-(1,2,5-Trimethyl-1*H*-pyrrol-3-yl)-1,4-naphthoquinone (**8c**).

This compound was obtained as a red solid (42%), mp 162-163 °C; ^{1}H nmr ($CDCl_3$): δ 2.26 (s, 3H), 2.32 (s, 3H), 3.45 (s, 3H), 6.20 (s, 1H), 6.80 (s, 1H), 7.70-7.75 (m, 2H), 8.07-8.17 (m, 2H); ms (isobutane) m/z 266 (MH^+); uv (THF) λ_{max} (lg ε) = 248 (4.15), 295 (4.04), 502 (3.53); ir (KBr) ν 1640, 1670 cm^{-1} (C=O); hrms (FAB) m/z Calcd. for $C_{17}H_{16}NO_2$ (MH^+): 266.1181; Found: 266.1177.

Methyl 4-(1,4-dioxo-1,4-dihydronaphthalen-2-yl)-1,2,5-trimethyl-1*H*-pyrrole-3-carboxylate (**8d**).

This compound was obtained as a orange solid (51%), mp 184-186 °C; ^{1}H nmr ($CDCl_3$): δ 2.22 (s, 3H), 2.53 (s, 3H), 3.47 (s, 3H), 3.57 (s, 3H), 6.70 (s, 1H), 7.71-7.78 (m, 2H), 8.08-8.15 (m, 2H); ms (isobutane) m/z 323 (M^+); uv (THF) λ_{max} (lg ε) = 244 (4.08), 263 (3.96), 294 (3.64), 322 (3.46), 452 (3.14); ir (KBr) ν 1660, 1670 cm^{-1} (C=O, quinone), 1710 cm^{-1} (C=O, ester); hrms (FAB) m/z Calcd. for $C_{19}H_{18}NO_4$ (MH^+): 324.1236; Found: 324.1234.

2-(2,5-Dimethyl-1*H*-pyrrol-3-yl)-5-hydroxy-1,4-naphthoquinone (**9a**).

This compound was obtained as a black solid (37%), mp 195-196 °C; ^{1}H nmr (DMSO-d_6): δ 2.16 (s, 3H), 2.30 (s, 3H), 6.13 (m, 1H), 6.68 (s, 1H), 7.29 (dd, 1H, J = 1.0 Hz, J = 8.4 Hz), 7.48 (dd, 1H, J = 1.0 Hz, J = 7.4 Hz), 7.72 (dd, 1H, J = 7.4 Hz, J = 8.4 Hz), 10.98 (s, 1H), 12.11 (s, 1H); ms (isobutane) m/z 268 (MH^+); uv (THF) λ_{max} (lg ε) = 240 (4.10), 292 (3.97), 402 (3.70), 532 (3.49); ir (KBr) ν 3260 cm^{-1} (N-H), 1620 cm^{-1} (C=O); hrms (FAB) m/z Calcd. for $C_{16}H_{14}NO_3$ (MH^+): 268.0974; Found: 268.0971.

Methyl 4-(5-Hydroxy-1,4-dioxo-1,4-dihydronaphthalen-3-yl)-2,5-dimethyl-1*H*-pyrrol-2-yl-carboxylate (**9b**).

This compound was obtained as a orange solid (31%), mp 182-183 °C; ^{1}H nmr ($CDCl_3$): 2.18 (s, 3H), 2.49 (s, 3H), 3.64 (s, 3H), 6.74 (s, 1H), 7.23-7.30 (m, 1H), 7.62-7.66 (m, 2H), 8.55 (s, 1H), 12.11 (s, 1H); ms (isobutane) m/z 325 (M^+); uv (THF) λ_{max} (lg ε) = 244 (4.04), 259 (4.04), 412 (3.58); ir (KBr) ν 3260 cm^{-1} (N-H), 1635, 1670 cm^{-1} (C=O, quinone), 1725 cm^{-1} (C=O, ester); hrms (FAB) m/z Calcd. for $C_{18}H_{16}NO_5$ (MH^+): 326.1028; Found: 326.1027.

2-(1,2,5-Trimethyl-1*H*-pyrrol-3-yl)-5-hydroxy-1,4-naphthoquinone (**9c**).

This compound was obtained as a black solid (33%), mp 181-182 °C; ^{1}H nmr ($CDCl_3$): 2.26 (s, 3H), 2.33 (s, 3H), 3.46 (s, 3H), 6.20 (s, 1H), 6.74 (s, 1H), 7.22-7.29 (m, 1H), 7.61-7.65 (m, 2H), 12.32 (s, 1H); ms (isobutane) m/z 282 (MH^+); uv (THF) λ_{max} (lg ε) = 240 (3.88), 290 (3.66), 406 (3.49), 521 (3.21); ir (KBr) ν 1630 cm^{-1} (C=O); hrms (FAB) m/z Calcd. for $C_{17}H_{16}NO_3$ (MH^+): 282.1130; Found: 282.1136.

Methyl 4-(5-Hydroxy-1,4-dioxo-1,4-dihydronaphthalen-3-yl)-1,2,5-trimethyl-1*H*-pyrrol-2-yl-carboxylate (**9d**).

This compound was obtained as a orange solid (26%), mp 172-174 °C; ^{1}H nmr ($CDCl_3$): 2.22 (s, 3H), 2.54 (s, 3H), 3.48 (s, 3H), 3.59 (s, 3H), 6.72 (s, 1H), 7.24-7.30 (m, 1H), 7.62-7.75 (m, 2H), 12.10 (s, 1H); ms (isobutane) m/z 339 (M^+); uv (THF) λ_{max} (lg ε) = 242 (3.79), 264 (3.76), 409 (3.24); ir (KBr) ν 1640, 1660 cm^{-1} (C=O, quinone), 1705 cm^{-1} (C=O, ester); hrms (FAB) m/z Calcd. for $C_{19}H_{18}NO_5$ (MH^+): 340.1185; Found: 340.1201.

Synthesis of Compounds (**10** and **11**).

Methyl 4-(1,2-Dioxo-1,2-dihydronaphthalen-4-yl)-2,5-dimethyl-1*H*-pyrrol-3-yl-carboxylate (**10**).

A solution of pyrrole (**7b**, 3.27 mmoles, 500 mg) and 1,2-naphthoquinone (**3**, 6.53 mmoles, 1.033 g) in absolute ethyl alcohol (50 mL) was stirred with a trace of *p*-toluenesulfonic acid for three hours. In the same way as above, compound (**10**, 724 mg, 72%) is obtained as a red solid, mp 176-179 °C; ^{1}H nmr ($CDCl_3$): δ 2.20 (s, 3H), 2.57 (s, 3H), 3.48 (s, 3H), 6.33 (s, 1H), 7.23 (m, 1H), 7.44-7.61 (m, 2H), 8.11-8.17 (m, 1H), 8.72 (s, 1H); ms (ammonia) m/z 327 (MNH_4^+), 310 (MH^+); uv (THF) λ_{max} (lg ε) = 246 (4.12), 315 (3.42), 398 (3.23); ir (KBr) ν 3280 cm^{-1} (N-H), 1650, 1690 cm^{-1} (C=O, quinone), 1735 cm^{-1} (C=O, ester); hrms (FAB) m/z Calcd. for $C_{18}H_{16}NO_4$ (MH^+): 310.1079; Found: 310.1069.

Methyl 4-(1,2-Dioxo-1,2-dihydronaphthalen-4-yl)-1,2,5-trimethyl-1*H*-pyrrol-3-yl-carboxylate (**11**).

As above, pyrrole (**7d**, 2.99 mmoles, 500 mg) and 1,2-naphthoquinone (**3**, 6 mmoles, 950 mg), give compound (**11**, 606 mg, 65%) as a red solid, mp 188-189 °C; ^{1}H nmr ($CDCl_3$): δ 2.17 (s, 3H), 2.58 (s, 3H), 3.40 (s, 3H), 3.51 (s, 3H), 6.27 (s, 1H), 7.15-7.19 (m, 1H), 7.38-7.53 (m, 2H), 8.09-8.13 (m, 1H); ms (ammonia) m/z 324 (MH^+); uv (THF) λ_{max} (lg ε) = 248 (4.26), 330 (3.42), 398 (3.26); ir (KBr) ν 1660, 1690 cm^{-1} (C=O, quinone), 1720 cm^{-1} (C=O, ester).

Synthesis of Quinoline-5,8-dione (**4**).

Quinone (**4**) is obtained by the method described in the literature [7] from 8-hydroxyquinoline in three steps (yield: 29%), mp 121-122 °C. Lit. [7]: 121-122 °C.

Synthesis of Quinoxaline-5,8-dione (**5**) [9-15].

a) Nitration of 1,4-dimethoxybenzene leads a mixture of 2,3- and 2,5-dinitro-1,4-dimethoxybenzene (ratio 18/81) which by reduction and reaction with glyoxal leads to 5,8-dimethoxyquinoxaline.

b) The reduction of the above mixture of dinitro-1,4-dimethoxybenzenes by tin in concentrated HCl following the described method [12] gives after reaction with glyoxal 5,8-dimethoxyquinoxaline in 47% yield on the basis of 2,5-dinitro-1,4-dimethoxybenzene. Catalytic reduction by hydrogen [11] affords only 34% yield of the same 5,8-dimethoxyquinoxaline, mp 150-151 °C. Lit. [11]: 150-151 °C, but the product is easier to isolate.

c) Oxidative demethylation by CAN. The above 5,8-dimethoxyquinoxaline (26.3 mmoles, 5 g) in acetonitrile (100 mL) was stirred for one hour with CAN (66.7 mmoles, 36.15 g). Extraction by chloroform (3 X 100 mL) leads to compound (**5**, 3.12 g, 74%), mp 172-173 °C. Lit. [11]: 172-173 °C.

General Method for the Synthesis of 6-Pyrrolylquinoline-5,8-diones (**12a**-**12d**) and 6-Pyrrolylquinoxaline-5,8-diones (**13a**-**13d**).

A solution of $FeCl_3 \bullet 6H_2O$ (3.14 mmoles, 912 mg) in water (48 mL) and acetic acid (12 mL) was stirred with 3.14 mmoles of quinoline-5,8-dione (**4**) or quinoxaline-5,8-dione (**5**) and 12.58 mmoles of pyrrole (**7**) in chloroform (50 mL). The reaction was followed by tlc; the mixture was isolated as above.

6-(4-Carbomethoxy-2,5-dimethylpyrrol-3-yl)quinoline-5,8-dione (**12b**).

This compound was obtained as a black solid (19%), mp 220-221 °C; ^{1}H nmr ($CDCl_3$): δ 2.25 (d, 3H, J = 0.7 Hz), 2.34 (s, 3H), 3.46 (s, 3H), 6.22 (d, 1H, J = 0.7 Hz), 6.97 (s, 1H), 7.66 (dd, 1H, J = 7.9 Hz, J = 4.7 Hz), 8.47 (dd, 1H, J = 7.9 Hz, J = 1.7 Hz), 9.03 (dd, 1H, J = 4.7 Hz, J = 1.7 Hz); ^{13}C nmr ($CDCl_3$): 12.4, 12.6, 30.7, 108.2, 112.6, 127.1, 129.5, 129.6, 131.1, 131.2, 134.9, 144.1, 147.8, 154.2, 183.6, 185.2; ms (70 eV) m/z 266 ($M^{+\bullet}$); uv (THF) λ_{max} (lg ε) = 250 (4.12), 293 (3.87), 382 (3.32), 510 (3.51); ir (KBr) ν 1650, 1670 cm^{-1} (C=O); hrms (FAB) m/z Calcd. for $C_{16}H_{15}N_2O_2$ (MH^+): 267.1134; Found: 267.1133.

6-(1,2,5-Trimethylpyrrol-3-yl)quinoline-5,8-dione (**12c**).

This compound was obtained as a red solid (59%), mp 237-241 °C; ^{1}H nmr ($CDCl_3$): δ 2.25 (s, 3H), 2.52 (s, 3H), 3.63 (s, 3H), 6.94 (s, 1H), 7.70 (dd, 1H, J = 7.9 Hz, J = 4.7 Hz), 8.48 (dd, 1H, J = 7.9 Hz, J = 1.7 Hz), 9.05 (dd, 1H, J = 4.7 Hz, J = 1.7 Hz); ms (70 eV) m/z 310 ($M^{+\bullet}$); uv (THF) λ_{max} (lg ε) = 240 (4.21), 288 (3.66), 462 (3.17); ir (KBr) ν 3360 cm^{-1} (N-H), 1660, 1670 cm^{-1} (C=O, quinone), 1705 cm^{-1} (C=O, ester); hrms (FAB) m/z Calcd. for $C_{17}H_{17}N_2O_4$ (MH^+): 313.1188; Found: 313.1184.

6-(4-Carbomethoxy-1,2,5-trimethylpyrrol-3-yl)quinoline-5,8-dione (**12d**).

This compound was obtained as a red solid (22%), mp 171-172 °C; ^{1}H nmr ($CDCl_3$): δ 2.19 (s, 3H), 2.49 (s, 3H), 3.45 (s, 3H), 3.55 (s, 3H), 6.86 (s, 1H), 7.66 (dd, 1H, J = 7.9 Hz, J = 4.7 Hz), 8.42 (dd, 1H, J = 7.9 Hz, J = 1.7 Hz), 9.00 (dd, 1H, J = 4.7 Hz, J = 1.7 Hz); ms (ammonia) m/z 325 (MH^+); uv (THF) λ_{max} (lg ε) = 240 (4.38), 286 (3.79), 456 (3.14); ir (KBr) ν 1660, 1670 cm^{-1} (C=O, quinone), 1700 cm^{-1} (C=O, ester).

6-(4-Carbomethoxy-2,5-dimethylpyrrol-3-yl)quinoxaline-5,8-dione (**13b**).

This compound was obtained as a red solid (44%), mp 209-210 °C; ^{1}H nmr (CDCl$_3$): δ 2.27 (s, 3H), 2.51 (s, 3H), 3.65 (s, 3H), 7.00 (s, 1H), 8.36 (s, 1H), 9.05 (m, 2H); ms (ammonia) m/z 312 (MH$^+$); uv (THF) λ_{max} (lg ε) = 251 (4.26), 286 (3.91), 330 (3.60), 468 (3.25); ir (KBr) ν 1655, 1690 cm^{-1} (C=O, quinone), 1705 cm^{-1} (C=O, ester); hrms (FAB) m/z Calcd. for $C_{16}H_{14}N_3O_4$ (MH$^+$): 312.0984; Found: 312.0990.

6-(1,2,5-Trimethylpyrrol-3-yl)quinoxaline-5,8-dione (**13c**).

This compound was obtained as a red solid (56%), mp 196-197 °C; ^{1}H nmr (CDCl$_3$): δ 2.26 (s, 3H), 2.36 (s, 3H), 3.47 (s, 3H), 6.26 (s, 1H), 7.04 (s, 1H), 9.01 (m, 2H); ms (ammonia) m/z 268 (MH$^+$); uv (THF) λ_{max} (lg ε) = 248 (4.23), 282 (4.23), 349 (3.92), 519 (3.73); ir (KBr) ν 1640, 1690 cm^{-1} (C=O, quinone); hrms (FAB) m/z Calcd. for $C_{15}H_{14}N_3O_2$ (MH$^+$): 268.1086; Found: 268.1088.

6-(4-Carbomethoxy-1,2,5-trimethylpyrrol-3-yl)quinoxaline-5,8-dione (**13d**).

This compound was obtained as a red solid (61%), mp 235-237 °C; ^{1}H nmr (CDCl$_3$): δ 2.26 (s, 3H), 2.54 (s, 3H), 3.50 (s, 3H), 3.62 (s, 3H), 6.97 (s, 1H), 9.04 (m, 2H); ms (ammonia) m/z 326 (MH$^+$); uv (THF) λ_{max} (lg ε) = 251 (4.23), 277 (4.09), 324 (3.70), 464 (3.21); ir (KBr) ν 1662, 1690 cm^{-1} (C=O, quinone), 1708 cm^{-1} (C=O, ester); hrms (FAB) m/z Calcd. for $C_{17}H_{16}N_3O_4$ (MH$^+$): 326.1141; Found: 326.1138.

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