Regioselective 6-Amination and 6-Arylation of 5,8-Quinolinedione Promoted by Metal Ions

Katsuhira Yoshida,* Miwa Ishiguro, Hiroyuki Honda, Mayumi Yamamoto, and Yuji Kubo
Department of Chemistry, Faculty of Science, Kochi University, Akebono-cho, Kochi 780
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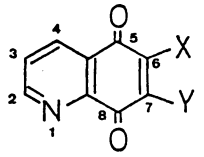
The effects of some metal ions on the amination and arylation of 5,8-quinolinedione (**1**) and on the amine displacement of 6-piperidino-5,8-quinolinedione have been investigated. The reaction of **1** with various amines in chloroform or ethanol was specifically promoted by Ni(II) ions to give selectively the corresponding 6-(substituted amino)-5,8-quinolinediones. With *N,N*-dialkylanilines in acetic acid the reaction was strongly promoted by Cu(II) ions to give exclusively 6-arylated products, 6-[*p*-(dialkylamino)phenyl]-5,8-quinolinediones. The metal chelate complex was proposed as an activated intermediate.

It is generally known that the reactivities and electronic structures of organic ligands are affected by coordination to metal ions. In recent papers, we have reported novel direct alkylaminations of various α-substituted anthraquinones in the presence of metal ions.[1] The formation of a metal chelate complex, in which the α-substituent and the neighboring oxygen atom of the quinone carbonyl group coordinate to the metal ion, was proposed to increase the electrophilicity of the anthraquinone nucleus and to facilitate the ocurrence of direct alkylamination.

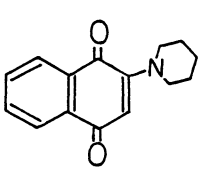
A strong activation effect induced by metal chelate formation has also been found in the reactions of various amines with 5,8-quinolinedione (**1**), giving 6-aminated and 6-arylated products selectively.[2] In this paper, we report on details of the effect of metal ions on the reaction of 5,8-quinolinediones with various amines. The spectral features for metal chelate formation upon the addition of the metal salts to solutions of substituted 5,8-quinolinediones were also investigated.



	X	Y
1	H	H
2	Piperidino	H
3	H	Piperidino
4	*n*-BuNH	H
5	H	*n*-BuNH
6	*p*-$(CH_3)_2N$-C_6H_4-NH	H
7	H	*p*-$(CH_3)_2N$-C_6H_4-NH
8	*p*-CH_3O-C_6H_4-NH	H
9	H	*p*-CH_3O-C_6H_4-NH
10	*p*-Cl-C_6H_4-NH	H
11	*p*-O_2N-C_6H_4-NH	H
12	*p*-$(CH_3)_2N$-C_6H_4-	H
13	H	*p*-$(CH_3)_2N$-C_6H_4-
14	*p*-$(C_2H_5)_2N$-C_6H_4-	H
15	*p*-$(CH_3)NH$-C_6H_4-	H
16	*p*-$(C_4H_9)NH$-C_6H_4-	H
17	C_6H_5-$N(CH_3)$-	H
18	C_6H_5-$N(C_4H_9)$-	H

Results and Discussion

Amine Displacement of 6-Piperidino-5,8-quinolinedione (2) Catalyzed by Metal Ions. The reaction of 6-piperidino-5,8-quinolinedione (**2**) with butylamine was found to be catalyzed by some metal ions. As shown in Table 1, the reaction of **2** with butylamine gave 6-butylamino-5,8-quinolinedione (**4**); the amine exchange reaction proceeded at 30 °C in the presence of metal salts (Runs 2—7), but did not proceed at all in the absence of metal salt (Run 1). The catalytic activity of metal chlorides was found to be in the following order: Ni(II)≫Cu(II)>Co(II)>Al(III), Ce(III). The activity of Ni(II) ion was particularly superior to those of other metal ions. In the presence of 0.1 mole ratio of nickel(II) chloride, an 83% yield of **4** was obtained after 2.5 h (Run 5). Copper(II) chloride was less active than nickel(II) chloride; however, the yield of **4** was greatly improved and the reaction proceeded more rapidly with an increase in the amount of catalyst (Runs 2 and 3). Though the displacement of the piperidino group of **2** by butylamine proceeded smoothly in the presence of Ni(II) ions, an amine exchange reaction was not observed when 7-piperidino-5,8-quinolinedione (**3**) and 2-piperidino-1,4-naphthoquinone (**19**) were used instead of **2**, and the starting materials (**3** and **19**) were recovered.



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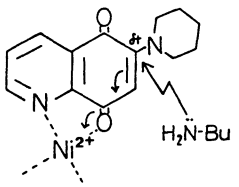

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Figure 1 shows the spectral changes observed upon an addition of nickel(II) chloride to a chloroform (10 vol% DMF) solutions of **2**. In the case of **2** the absorption maximum around 470 nm, due to a free ligand, was shifted to a longer wavelength with an increase in the absorption intensity. The maximum and constant absorbance were obtained over the range of the mole ratio of [Ni(II)]/[**2**]=0.8—2.0. We tested other metal

Table 1. Effect of Metal Chlorides on the Reaction of **2** with Butylamine[a)]

Run	Metal salt	Mole ratio [Metal salt]/[2]	Time h	Recovery/%[b)] **2**	Yield/%[b)] **4**
1	None	—	50	86	0
2	$CuCl_2$	0.1	25	Trace	43
3	$CuCl_2$	1.0	1	0	73
4	$CoCl_2$	0.1	45	4	43
5	$NiCl_2$	0.1	2.5	0	83
6	$AlCl_3$	0.1	25	Trace	7
7	$CeCl_3 \cdot 7H_2O$	0.1	33	Trace	19

a) Reactant **2** (0.5 g) was stirred in pyridine (15 ml) with butylamine (5 ml) and metal salt at 30 °C. b) Isolated yield after column chromatography.

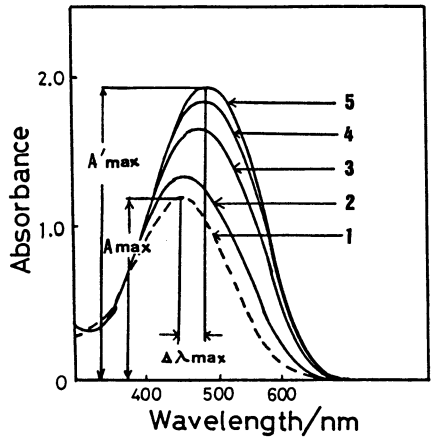


Fig. 1. Influence of added $NiCl_2$ on the absorption spectra of **2** in chloroform (10 vol% DMF) at 25 °C. $[2]_t=2.5\times10^{-4}$ M ([ ]$_t$ denotes the total concentration; 1 M=1 mol dm^{-3}); $[Ni(II)]_t=0.00$ (1), 5.0×10^{-5} (2), 1.0×10^{-4} (3), 1.5×10^{-4} (4), 2.0×10^{-4}—5.0×10^{-4} M (5).

Table 2. Influence of Added Metal Ions on the Absorption Spectra of **2** in Chloroform (10 vol% DMF) at 25 °C[a)]

Metal salt	Mole ratio [Metal salt]/[2]	λ'_{max} nm	$\Delta\lambda_{max}$[b)] nm	RA_{max}[c)]
None	—	470[a)]	—	—
$NiCl_2$	1.0	503	33	1.66
$CuCl_2$	1.0	500	30	1.64
$CoCl_2$	1.0	500	30	1.52

a) $[2]=2.5\times10^{-4}$ M; λ_{max}(free ligand)=470 nm, A_{max}(free ligand)= 1.206. b) $\Delta\lambda_{max}=\lambda'_{max}$(complex)$-\lambda_{max}$(free ligand). c) $RA_{max}=A'_{max}$(complex)$/A_{max}$(free ligand).

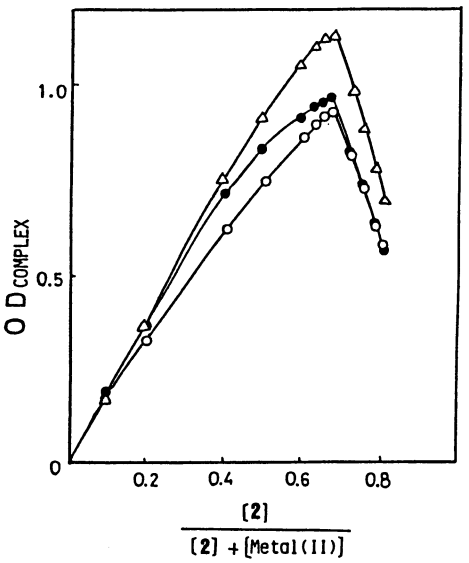


Fig. 2. Continuous variation plots at [2]+[Metal(II)]=2.5×10^{-4} M in chloroform(10 vol% DMF) at 25 °C.
—△—; $NiCl_2$, —●—; $CuCl_2$,—○—; $CoCl_2$.

ions (Cu(II) and Co(II)) and observed similar spectral changes. Table 2 summarizes the values of the bathochromic shift, $\Delta\lambda_{max}=\lambda'_{max}$ (complex)$-\lambda_{max}$ (free ligand), and the relative ratio of the absorption intensity, $RA_{max}=A'_{max}$ (complex)$/A_{max}$ (free ligand), calculated on the basis of spectral data. The values of $\Delta\lambda_{max}$ and RA_{max} for the metal ions are compatible with the order of catalytic activity in the amine exchange reaction. In Fig. 2, continuous-variation plots at [2]+[Metal(II)]=2.50×10^{-4} mol dm^{-3} are illustrated. The wavelengths (≈500 nm) at the absorption maxima of the metal complexes were employed. Figure 2 clearly shows that maxima appear at [2]/([2]+[Metal(II)])= 0.67, supporting the formation of 2:1 (Compound (**2**): Metal(II)) chelate complexes.

On the other hand, the spectral changes of compound **3** were fairly smaller than those of **2**, and the pattern of the changes was quite different from that observed in Fig. 1. Furthermore, in the case of **19** the absorption spectrum was not affected at all by the addition of nickel(II) salt. These results suggest that the formation of a metal chelate (**20**), in which the 1-nitrogen atom and the oxygen atom of the 8-carbonyl group of **2** coordinate to the metal ion, probably increases the electrophilicity of the 6-carbon atom and facilitates a nucleophilic substitution of the 6-piperidino group by butylamine. However, the formation of a similar metal chelate of **3** could not facilitate the displacement of the 7-piperidino group, probably because the electron density of the 7-carbon atom is not affected so much by metal chelate formation.

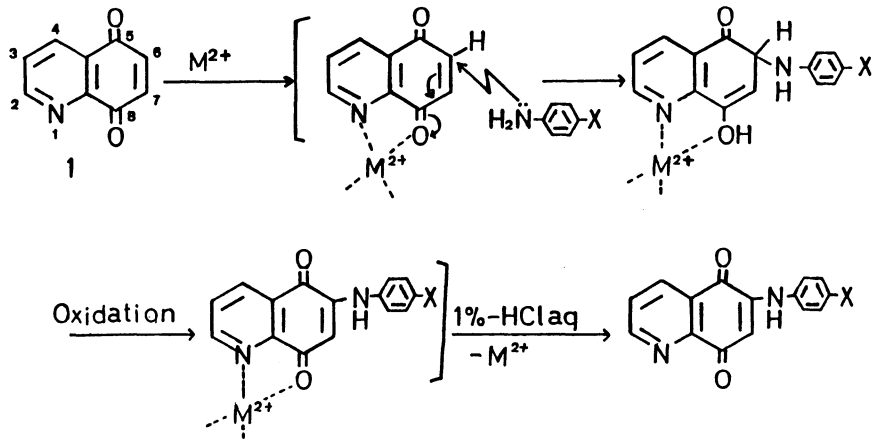
Regioselective 6-Amination of 5,8-Quinolinedione

(1) Catalyzed by Nickel(II) Ion. From the results of the catalytic action of metal ions in the amine exchange reaction of **2**, it is expected that nickel(II) ions can well catalyze the amination of **1** and the amino group would be preferentially introduced onto the 6-position of **1**. Therefore, we examined the reaction of **1** with various amines in the presence of nickel(II) chloride under atmospheric oxygen. The reaction of **1** with aromatic amines is already known to produce a mixture of 6- and 7-arylaminated products;[3,4] however, a reaction with aliphatic amines has not yet been reported. As shown in Table 3, in the absence of metal salt the reactions gave isomeric mixtures of the products, 6- and 7-amino derivatives of **1** (Runs 8, 10, 12, and 15). However, in the presence of nickel(II) chloride the regioselective and the regiospecific 6-amination of **1** were achieved in reactions with the aliphatic and primary aromatic amines, respectively (Runs 9, 11 and 13, 16, 17, 19). The reaction was considerably affected by the amounts of nickel(II) chloride, especially when strong electron-donating amino groups were introduced, more than a half molar ratio of the metal salt to **1** was needed. This suggests that the metal ion is preferentially combined with the aminated product rather than with **1** and that, consequently, the catalytic action of the metal ion is prohibited. When the reaction was conducted under anaerobic conditions, the amination was suppressed considerably (Runs 13 and 14). Atmospheric oxygen plays an important role as an oxidizing agent for the completion of the amination of **1**; the adducts formed by a Michael-type addition of amines to **1** can be dehydrogenated by both the unchanged **1** and atmospheric oxygen to give aminated products. The electrophilicity of 6-position of **1** would be so strongly increased by the formation of nickel(II) chelate that the 6-amination of **1** can proceed even in a reaction with *p*-nitroaniline (Runs 18 and 19). From the results described above, the mechanism of the regioselective 6-amination of **1** was proposed, as shown in Scheme 1.

Table 3. Effect of Added $NiCl_2$ on the Amination of 5,8-Quinolinedione (**1**)

Run	Amine	Mole ratio	Time	Product and yield/%[f]	
		$[Ni^{2+}]/[1]$	h	6-amino isomer	7-amino isomer
8[a]	Piperidine	None[d]	2.0[e]	**2** 48	**3** 10
9[a]	Piperidine	1.0	1.5[e]	**2** 75	**3** 6
10[b]	Butylamine	None[d]	2.0[e]	**4** 30	**5** 26
11[b]	Butylamine	0.5	1.5[e]	**4** 45	**5** 15
12[b]	*p*-(Dimethylamino)aniline	None[d]	6.0[e]	**6** 43	**7** 37
13[b]	*p*-(Dimethylamino)aniline	0.5	2.0	**6** 71	**7** 0
14[c]	*p*-(Dimethylamino)aniline	0.5	2.0[e]	**6** 32	**7** 0
15[b]	*p*-Methoxyaniline	None[d]	7.0[e]	**8** 28	**9** 28
16[b]	*p*-Methoxyaniline	0.5	2.0[e]	**8** 60	**9** 0
17[b]	*p*-Chloroaniline	0.5	3.0[e]	**10** 47	
18[b]	*p*-Nitroaniline	None[d]	15.0	No reaction	
19[b]	*p*-Nitroanilne	0.1	7.0[e]	**11** 36	

a) Reactant **1** (3.14 mmol) was stirred in chloroform (70 ml) at 0 °C with piperidine (9.42 mmol) and $NiCl_2$ under air atmosphere. b) Reactant **1** (3.14 mmol) was stirred in 95% ethanol (150 ml) at 30 °C with the substituted aniline (9.42 mmol) and $NiCl_2$ under air atmosphere. c) Reaction was conducted under argon atmosphere. d) Reactions were conducted without $NiCl_2$. e) Times for the whole starting material **1** was consumed. f) Isolated yield after column chromatography.



Scheme 1.

Table 4. Reaction of 5,8-Quinolinedione (**1**) with *N*-Alkyl- and *N,N*-Dialkylanilines in the Presence of Metal Salts[a)]

Run	Amine	Metal salt	Mole ratio [Metal salt]/[1]	Solvent	Time h	Product and yield/%[b)] 6-aryl isomer	7-aryl isomer	6-amino isomer
20	*N,N*-Dimethylaniline	None	—	AcOH	94.0	**12** 18	**13** 6	
21	*N,N*-Dimethylaniline	$NiCl_2$	0.5	EtOH	4.0	**12** 2.4	**13** 0	
22	*N N*-Dimethylaniline	$NiCl_2$	0.5	$CHCl_3$	7.5	**12** 2.4	**13** 0	
23	*N,N*-Dimethylaniline	$NiCl_2$	0.5	Pyridine	9.0	**12** Trace	**13** 0	
24	*N,N*-Dimethylaniline	$Ni(OAc)_2 \cdot 4H_2O$	0.5	AcOH	1.0	**12** 51	**13** 0	
25	*N,N*-Dimethylaniline	$Ni(OAc)_2 \cdot 4H_2O$	1.0	AcOH	1.0	**12** 62	**13** 0	
26	*N,N*-Dimethylaniline	$Cu(OAc)_2 \cdot H_2O$	1.0	AcOH	0.5	**12** 80	**13** 0	
27	*N,N*-Dimethylaniline	$Co(OAc)_2 \cdot 4H_2O$	1.0	AcOH	1.5	**12** 48	**13** 0	
28	*N,N*-Dimethylaniline	$Zn(OAc)_2 \cdot 2H_2O$	1.0	AcOH	5.5	**12** 32	**13** 0	
29	*N,N*-Dimethylaniline	$Ce(OAc)_3 \cdot H_2O$	1.0	AcOH	30.1	**12** 24	**13** 0	
30	*N,N*-Diethylaniline	$Cu(OAc)_2 \cdot H_2O$	1.0	AcOH	2.0	**14** 56		
31	*N*-Methylaniline	$Cu(OAc)_2 \cdot H_2O$	1.0	AcOH	0.5	**15** 12		**17** 61
32	*N*-Butylaniline	$Cu(OAc)_2 \cdot H_2O$	1.0	AcOH	1.0	**16** 40		**18** 29

a) Reactant **1** (1.0 g, 6.28 mmol) was stirred in the solvent (100 ml) with the amine (18.8 mmol) and metal salt at 30 °C. b) Isolated yields after column chromatography.

Regioselective 6-Arylation of 5,8-Quinolinedione (1) with *N*-Alkyl- and *N,N*-Dialkylanilines Promoted by Metal Ions. Griffiths et al. found that the reaction of 1,4-naphthoquinone with *N,N*-dialkylarylamines in acetic acid gave 2-[*p*-(dialkylamino)aryl]-1,4-naphthoquinones in 10—66% yields.[5)] As the structure of **1** is analogous to that of 1,4-naphthoquinone, **1** was expected to undergo the arylation by the reaction with *N,N*-dialkylarylamines. Hence, we examined the effects of metal ions on the reaction of **1** with some *N,N*-dialkyl- and *N*-alkylanilines in organic solvents. As shown in Table 4, in the absence of metal salt, the reaction of **1** with *N,N*-dimethylaniline in acetic acid proceeded slowly to give a mixture of 6- and 7-[*p*-(dimethylamino)phenyl]-5,8-quinolinediones (**12** and **13**) in low yields (Run 20). However, the reaction was strongly promoted by some metal ions and gave exclusively the 6-arylated products (Runs 24—29). Metal acetates were arranged in the order of activity as follows: Cu(II)>Ni(II)>Co(II)>Zn(II)≫Ce(III). The activity of Cu(II) ion was particularly superior to those of other metal ions in the arylation. The reaction was also drastically affected by the kind of solvent. The arylation hardly proceeded when ethanol, chloroform, or pyridine was used instead of acetic acid (Runs 21—23). In these solvents, **1** and *N,N*-dimethylaniline immediately formed a reddish purpule charge-transfer complex having an absorption maximum at ca. 510 nm, which was hardly affected by prolonged reaction time. On the contrary, in acetic acid the two reagents hardly form a charge-transfer complex, and gradually reacts to give arylated products. Similar solvent effects were also observed in the arylation of 1,4-naphthoquinone.[5)]

With *N*-alkylanilines, the reaction was also affected by the kind of solvent and metal salt. Pratt has already reported that the reaction of **1** with *N*-methylaniline in an alcohol solution gave a mixture of 6- and 7-(*N*-methylanilino)-5,8-quinolinediones in low yields, but in the presence of cerium(III) chloride the 6-amino isomer (**17**) was obtained exclusively in satisfactory yield.[3c)] In our case of using copper(II) acetate in acetic acid, however, the corresponding reaction gave the 6-arylated product,6-[*p*-(methylamino)phenyl]-5,8-quinolinedione (**15**), together with the 6-aminated product (**17**): the ratio of the yields was abuot 1 : 5 (Run 31). However, in a reaction with *N*-butylaniline the yield of the 6-arylated product (**16**) was higher than that of the corresponding 6-aminated product (**18**): the ratio was about 4 : 3 (Run 32). These results reveal that in a reaction of **1** with *N*-alkylanilines in acetic acid the regioselective 6-arylation competes with the 6-amination, and that the former proceeds predominantly along with an increase in the size of the alkyl residue of *N*-alkylaniline. The nucleophilic attack of the nitrogen atom of *N*-butylaniline would cause a considerable steric crowding in the transient state. The 6-arylation was presumably initiated by a nucleophilic attack of para-position of the benzene ring of the arylamine onto the electron deficient 6-position of **1** complexed with the metal ion, giving the 1,4-adduct and was completed by a subsequent oxidation of the adduct as the similar mechanism shown in Scheme 1.

Experimental

Measurements. All the melting points are uncorrected. The visible spectra were measured using a Hitachi 220A spectrometer. The ^1H NMR spectra were taken on a JEOL Model MH-100 spectrometer with TMS as the internal standard. The elemental analyses were measured on a Yanaco CHN recoder MT-2. Thin-layer chromatography was performed on silica gel (Merk Kieselgel 60) and the resulting chromatograms were measured on a chromatoscanner (Shimadzu CS-900).

Materials. 5,8-Quinolinedione (**1**) was prepared according to a procedure described in the literature.[6)] All of the metal chlorides and the metal acetates were reagent-grade and were used without further purification. All of the metal

perchlorate hexahydrates were prepared according to methods described in the literature.[7] The amines and the solvents were purified by ordinary methods.[8]

Reaction of 2 with Butylamine. The general procedure was as follows. To a solution of **2** (0.5 g, 2.06 mmol) and metal chloride (0—2.06 mmol) in 15 ml of pyridine was added 5 ml of butylamine dropwise with stirring at 30 °C. The reaction was monitored by TLC analysis. (silica gel/ethyl acetate); **2**: R_f=0.25, **4**: R_f=0.35. After the reaction, the solvent was removed under reduced pressure. To the residue was added a cold 1% hydrochloric acid solution; the product was then extracted with chloroform. The chloroform layer was washed with water, dried (Na_2SO_4), and then concentrated. The crude products were separated by column chromatography (silica gel: Wakogel C-300) using ethyl acetate as an eluent. The yields are summarized in Table 1.

Reaction of 1 with Various Amines. The general procedure was as follows. A solution of **1** (1 g, 6.28 mmol) in 100 ml of 95% ethanol was added to a solution of the amine (18.8 mmol) and $NiCl_2$ (0—6.28 mmol) in 50 ml of 95% ethanol with stirring in an open flask at 30 °C. The reaction was monitored by TLC analysis. After the reaction, the solvent was removed under reduced pressure. A cold 1% hydrochloric acid solution was added to the residue in order to decompose the nickel chelate complex of the aminated 5,8-quinolinediones. The aminated products were extracted with chloroform from an acidic solution containing a fine dispersed precipitate. The extraction was repeated several times. After the combined chloroform extracts had been washed with water, dried (Na_2SO_4), and concentrated, the crude products were separated by column chromatography (silica gel: Wakogel C-300) using ethyl acetate and/or chloroform as eluents. The yields are summarized in Table 3.

Reaction of 1 with *N*-Alkyl- and *N,N*-Dialkylanilines. A solution of **1** (1 g, 6.28 mmol) in 80 ml of acetic acid was slowly added to a solution of the *N*-substituted aniline (18.84 mmol) and metal salt (6.28 mmol) in 20 ml of acetic acid with stirring in an open flask at 30 °C. The reaction was monitored by TLC analysis. After the starting material **1** was consumed, the products were extracted with chloroform from the reaction solution. The extraction was repeated several times. After the combined chloroform extracts were washed with saturated sodium carbonate aqueous solution, washed further with water, dried (Na_2SO_4) and then concentrated in vacuo. The crude products were separated by column chromatography (silica gel: Wakogel C-300) using chloroform or ethyl acetate as eluents. The yields are summarized in Table 4.

Characterization and Identification of Products. Some properties of the compounds (**2**,[9] **10**,[3c] and **17**[3c]), were already known; these were identified by data described in the literature, together with the following additional data.

6-Piperidino-5,8-quinolinedione (2): mp 147—148 °C (lit,[9] 146—148 °C). λ_{max} (benzene) 462 nm (ε 3600). ^{1}H NMR ($CDCl_3$) δ=1.6—1.9 (6H, m, $(CH_2)_3$), 3.4—3.7 (4H, m, N-CH_2×2), 6.16 (1H, s, H^7), 7.54 (1H, dd, H^3), 8.30 (1H, dd, H^4), 8.95 (1H, dd, H^2). Found: C, 69.42; H, 6.09; N, 11.48%. Calcd for $C_{14}H_{14}N_2O_2$: C, 69.41; H, 5.82; N, 11.56%.

7-Piperidino-5,8-quinolinedione (3): mp 93—95 °C. λ_{max} (benzene) 465 nm (ε 3400). ^{1}H NMR ($CDCl_3$) δ=1.6—1.9 (6H, m, $(CH_2)_3$), 3.4—3.7 (4H, m, N-CH_2×2), 6.01 (1H, s, H^6), 7.55 (1H, dd, H^3), 8.33 (1H, dd, H^4), 8.86 (1H, dd, H^2). Found: C, 69.18; H, 6.03; N, 11.46%. Calcd for $C_{14}H_{14}N_2O_2$: C, 69.41; H, 5.82; N, 11.56%.

6-Butylamino-5,8-quinolinedione (4): mp 148—150 °C. λ_{max} (benzene) 446 nm (ε 3450). ^{1}H NMR ($CDCl_3$) δ=0.98 (3H, t, CH_3), 1.1—1.9 (4H, m, $(CH_2)_2$), 3.21 (2H, q, NH-CH_2), 5.86 (1H, b, NH), 5.90 (1H, s, H^7), 7.53 (1H, dd, H^3), 8.34 (1H, dd, H^4), 8.97 (1H, dd, H^2). Found: C, 68.17; H, 6.42; N, 12.19%. Calcd for $C_{13}H_{14}N_2O_2$: C, 67.81; H, 6.13; N, 12.17%.

7-Butylamino-5,8-quinolinedione (5): mp 139—141 °C. λ_{max} (benzene) 447 nm (ε 3100). ^{1}H NMR ($CDCl_3$) δ=0.98 (3H, t, CH_3), 1.1—1.9 (4H, m, $(CH_2)_2$), 3.22 (2H, q, NH-CH_2), 5.76 (1H, s, H^6), 6.10 (1H, b, NH), 7.63 (1H, dd, H^3), 8.43 (1H, dd, H^4), 8.89 (1H, dd, H^2). Found: C, 67.58; H, 6.35; N, 12.20%. Calcd for $C_{13}H_{14}N_2O_2$: C, 67.81; H, 6.13; N, 12.17%.

6-[*p*-(Dimethylamino)anilino]-5,8-quinolinedione (6): mp 207—209 °C. λ_{max} (benzene) 543 nm (ε 3800). ^{1}H NMR ($CDCl_3$) δ=2.94 (6H, s, CH_3×2), 6.40 (1H, s, H^7), 6.70 (2H, d, benzene ring), 7.12 (2H, d, benzene ring), 7.40 (1H, b, NH), 7.54 (1H, dd, H^3), 8.39 (1H, dd, H^4), 8.99 (1H, dd, H^2). Found: C, 69.41; H, 5.41; N, 14.57%. Calcd for $C_{17}H_{15}N_3O_2$: C, 69.61; H, 5.15; N, 14.33%.

7-[*p*-(Dimethylamino)anilino]-5,8-quinolinedione (7): mp 223—225 °C. λ_{max} (benzene) 542 nm (ε 3700). ^{1}H NMR ($CDCl_3$) δ=2.95 (6H, s, CH_3×2), 6.25 (1H, s, H^6), 6.71 (2H, d, benzene ring), 7.14 (2H, d, benzene ring), 7.60 (1H, b, NH), 7.63 (1H, dd, H^3), 8.40 (1H, dd, H^4), 8.92 (1H, dd, H^2). Found: C, 69.57; H, 5.36; N, 14.17%. Calcd for $C_{17}H_{15}N_3O_2$: C, 69.61; H, 5.15; N, 14.33%.

6-(*p*-Anisidino)-5,8-quinolinedione (8): mp 256—259 °C. λ_{max} (benzene) 483 nm (ε 4500). ^{1}H NMR ($CDCl_3$) δ=3.78 (3H, s, OCH_3), 6.35 (1H, s, H^7), 6.87 (2H, d, benzene ring), 7.14 (2H, d, benzene ring), 7.35 (1H, b, NH), 7.54 (1H, dd, H^3), 8.34 (1H, dd, H^4), 8.95 (1H, dd, H^2). Found: C, 68.50; H, 4.51; N, 10.02%. Calcd for $C_{16}H_{12}N_2O_3$: C, 68.57; H, 4.32; N, 9.99%.

7-(*p*-Anisidino)-5,8-quinolinedione (9): mp 200—203 °C. λ_{max} (benzene) 483 nm (ε 3600). ^{1}H NMR ($CDCl_3$) δ=3.79 (3H, s, OCH_3), 6.18 (1H, s, H^6), 6.88 (2H, d, benzene ring), 7.15 (2H, d, benzene ring), 7.52 (1H, b, NH), 7.60 (1H, dd, H^3), 8.36 (1H, dd, H^4), 8.88 (1H, dd, H^2). Found: C, 68.47; H, 4.55; N, 10.15%. Calcd for $C_{16}H_{12}N_2O_3$: C, 68.57; H, 4.32; N, 9.99%.

6-(*p*-Chloroanilino)-5,8-quinolinedione (10): mp 239—240 °C (lit,[3c] 237—238 °C). λ_{max} (benzene) 466 nm (ε 3900). ^{1}H NMR (DMSO-d_6) δ=6.16 (1H, s, H^7), 7.38 (4H, s, benzene ring), 7.51 (1H, dd, H^3), 8.35 (1H, dd, H^4), 8.93 (1H, dd, H^2), 9.24 (1H, b, NH). Found: C, 63.87; H, 3.55; N, 9.78%. Calcd for $C_{15}H_9N_2O_2Cl$: C, 63.28; H, 3.19, N, 9.84%.

6-(*p*-Nitroanilino)-5,8-quinolinedione (11): mp 278 °C (decomp). λ_{max} (benzene) 447 nm (ε 6500). ^{1}H NMR (CF_3COOD) δ=6.93 (1H, s, H^7), 7.66 (2H, d, benzene ring), 8.45 (2H, d, benzene ring), 8.50 (1H, dd, H^3), 9.25 (1H, dd, H^4), 9.35 (1H, dd, H^2). Found: C, 61.06; H, 3.39; N, 14.24%. Calcd for $C_{15}H_9N_3O_4$: C, 61.02; H, 3.07; N, 14.23%.

6-[*p*-(Dimethylamino)phenyl]-5,8-quinolinedione (12): mp 204—206 °C. λ_{max} (benzene) 535 nm (ε 7800). ^{1}H NMR ($CDCl_3$) δ=3.02 (6H, s, CH_3×2), 6.70 (2H, d, benzene ring), 7.12 (1H, s, H^7), 7.56 (2H, d, benzene ring), 7.62 (1H, dd, H^3), 8.41 (1H, dd, H^4), 8.98 (1H, dd, H^2). Found: C, 73.60; H, 4.78; N, 10.14%. Calcd for $C_{17}H_{14}N_2O_2$: C, 73.37; H, 5.07; N, 10.07%.

7-[*p*-(Dimethylamino)phenyl]-5,8-quinolinedione (13):

λ_{max} (benzene) 536 nm (ε 7760). ^{1}H NMR ($CDCl_3$) δ=3.06 (6H, s, CH_3×2), 6.76 (2H, d, benzene ring), 7.09 (1H, s, H^6), 7.66 (2H, d, benzene ring), 7.66 (1H, dd, H^3), 8.42 (1H, dd, H^4), 9.055 (1H, dd, H^2). Found: C, 73.19; H, 4.91; N, 9.89%. Calcd for $C_{17}H_{14}N_2O_2$: C, 73.37; H, 5.07; N, 10.07%.

6-[*p*-(Diethylamino)phenyl]-5,8-quinolinedione (14): mp 136—137 °C. λ_{max} (benzene) 551 nm (ε 8700). ^{1}H NMR ($CDCl_3$) δ=1.20 (6H, t, CH_3×2), 3.44 (4H, q, CH_2×2), 6.72 (2H, d, benzene ring), 7.18 (1H, s, H^7), 7.62 (2H, d, benzene ring), 7.62 (1H, dd, H^3), 8.50 (1H, dd, H^4), 9.04 (1H, dd, H^2). Found: C, 74.20: H, 5.50; N, 8.57%. Calcd for $C_{19}H_{18}N_2O_2$: C, 74.23; H, 5.90; N, 9.14%.

6-[*p*-(Methylamino)phenyl]-5,8-quinolinedione (15): mp 248—250 °C. λ_{max} (benzene) 511 nm (ε 7410). ^{1}H NMR ($CDCl_3$) δ=2.88 (3H, s, CH_3), 4.13 (1H, b, NH), 6.65 (2H, d, benzene ring), 7.18 (1H, s, H^7), 7.57 (2H, d, benzene ring), 7.66 (1H, dd, H^3), 8.49 (1H, dd, H^4), 9.03 (1H, dd, H^2).

6-[*p*-(Butylamino)phenyl]-5,8-quinolinedione (16): mp 141—142 °C. λ_{max} (benzene) 515 nm (ε 7300). ^{1}H NMR ($CDCl_3$) δ=0.96 (3H, t, CH_3), 1.2—1.8 (4H, m, $(CH_2)_2$), 3.18 (2H, t, NH-CH_2), 4.16 (1H, b, NH), 6.65 (2H, d, benzene ring), 7.16 (1H, s, H^7), 7.57 (2H, d, benzene ring), 7.69 (1H, dd, H^3), 8.48 (1H, dd, H^4), 9.04 (1H, dd, H^2). Found: C, 74.20, H, 5.73; N, 8.65%. Calcd for $C_{19}H_{18}N_2O_2$: C, 74.49; H, 5.92; N, 9.14%.

6-(*N*-Methylanilino)-5,8-quinolinedione (17): mp 178—180 °C (lit,[3c] 181—182 °C). λ_{max} (benzene) 460 nm (ε 3800). ^{1}H NMR ($CDCl_3$) δ=3.44 (3H, s, CH_3), 6.23 (1H, s, H^7), 7.05—7.5 (5H, m, benzene ring), 7.56 (1H, dd, H^3), 8.21 (1H, dd, H^4), 8.98 (1H, dd, H^2). Found: C, 72.74; H, 4.29; N, 10.49%. Calcd for $C_{16}H_{12}N_2O_2$: C. 72.72; H, 4.58; N, 10.60%.

6-(*N*-Butylanilino)-5,8-quinolinedione (18): mp 141—143 °C. λ_{max} (benzene) 470 nm (ε 3600). ^{1}H NMR ($CDCl_3$) δ=0.93 (3H, t, CH_3), 1.1—1.9 (4H, m, $(CH_2)_2$), 3.79 (2H, t, N-CH_2), 6.21 (1H, s, H^7), 7.0—7.5 (5H, m, benzene ring), 7.53 (1H, dd, H^3), 8.23 (1H, dd, H^4), 8.96 (1H, dd, H^2).

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