Quinone Chemistry. Reaction of 2,3-Dichloro-1,4-naphthoquinone with 2-Aminophenols in Pyridine

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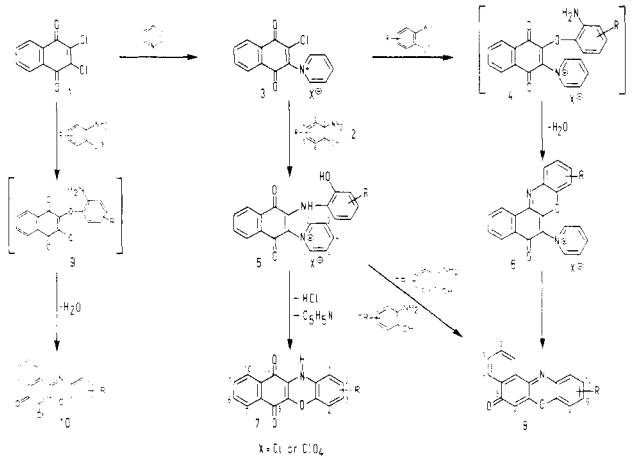
The reaction of 2,3-dichloro-1,4-naphthoquinone (1) and 2-aminophenols (2) in pyridine furnished substituted 6-chloro-5*H*-benzo[*a*]phenoxazin-5-one (**10**), 5*H*-benzo[*a*]phenoxazin-5-one (**8**), 5*H*-benzo[*a*]phenoxazin-5-one-6-pyridinium chloride (**6**), 2-(2-hydroxyanilino)-1,4-naphthoquinone-3-pyridinium chloride (**5**), and 12*H*-benzo[*b*]phenoxazine-6,11-dione (**7**). It was observed that the nature and yields of the reaction products were greatly influenced by the substituent present in **2**. The reaction mechanism for the formation of all products is discussed, and spectroscopic data are also given. This reaction for the first time led to a development of a novel, convenient synthesis of a new class of heterocyclic quinones (**7**).

In continuation of our investigations of quinone[1-4] and phenoxazone chemistry,[5-10] we have studied the reactions of benzoquinones and naphthoquinones with 2-aminophenols. In a preceding paper of this series[11] the reaction of 2,3-dichloro-1,4-naphthoquinone (1) with 2-aminophenols (2) in alcohol was investigated. The structures described earlier[16,17] were corrected, new structures were assigned, and a mechanism for the formation of these products was presented. This work resulted in a new high-yield synthesis of substituted 6-chloro-5*H*-benzo[*a*]-phenoxazin-5-ones. It was thus of interest to examine the reaction of **1** with **2** in pyridine especially because also in this reaction unexpected results[16] are described.

It was reported[16] that **1** reacts with **2a** in pyridine to give 5*H*-benzo[*a*]phenoxazin-5-one (**8a**) in 42% yield; the authors also claimed to have obtained **8a** in quantitative yield by treatment of 6-chloro-5-hydroxy-12*H*-benzo[*a*]phenoxazine (A) with pyridine. Despite intensive efforts we could not verify the yield of **8a** in the former reaction, and the latter appears to be improbable because we already have shown[11] that A is a highly unstable compound, so this was not the starting material used by Van Allan and Reynolds[16] for this reaction. The reaction mechanism suggested seems also not to be reliable. The authors have not mentioned how the formation of **8a** took place and at which stage of the reaction pyridine was added to the reactants or intermediates. It is also unclear[16] how the second chlorine atom of **1** is replaced by hydrogen during the formation of **8a**. The purpose of our work was, therefore, to reinvestigate the complex reaction of **1** and **2a** in pyridine and to establish the structure of the reaction products and their mechanism of formation. We have also examined in detail any changes in the yield and nature of products with different substituents in **2a**. This investigation led for the first time to a novel, convenient synthesis of a new class of heterocyclic quinones (**7**) containing electron-withdrawing substituents. The overall general reactions are presented in Scheme I, and yields of the reaction products are given in Table I.

Scheme I



From our study the reaction of **1** and **2** proceeds as follows. In the main reaction, **1** with pyridine yields a quaternary pyridinium salt **3**. This intermediate reacts further with **2** in two main directions. (i) Nucleophilic displacement of the chlorine atom in **3** by the amino group of **2** furnishes **5**, which on elimination of hydrogen chloride and pyridine leads to the formation of a new class of heterocyclic quinones (**7**). On the other hand, **5** in a 2-aminophenol exchange reaction using a second molecule of 2-aminophenol can also yield **8**. (ii) Nucleophilic attack of the phenoxide anion on **3** yields the possible intermediate **4** which leads to **6** by the elimination of water. Loss of the pyridine ring from **6** affords **8**. In a side reaction the phenoxide anion of **2** displaces one chlorine atom of **1** to yield an intermediate of type **9** which on subsequent ring closure forms **10**. Proofs of the structures of the products were based firmly on elemental analyses, UV, IR, ^{1}H NMR, and mass spectra, chemical reactions, or comparison with authentic samples.

Several times the reaction of **1** and **2a** in pyridine was repeated under the described[16] conditions, but we were

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Table I. Product Yields (%) for the Reaction of 2,3-Dichloro-1,4-naphthoquinone (1) and 2-Aminophenols (2)

	reactant									
product	2a, R = H	2b, R = 4-CH_3	2c[a]	2d, R = 4-COOH	2e, R = 4-Cl	2f, R = 4,6-Cl_2	2g, R = 4-NO_2	2h, R = 5-NO_2	2i, R = 3-$COCH_3$	2j, R = 3,4,6-Cl_3
5	13	*d*	*d*		*d*	*d*	*d*	*d*	*d*	*d*
6	6	*d*	40	16[b]	9	*d*	*d*	*d*	*d*	*d*
7	*c*	*c*	*c*	*c*	1.5	33	47	65.5	47	92
8	10	5.5	2.6	*d*	7	0.9	1.7	1.3	*c*	*c*
10	0.5	0.5	0.1	*d*	2	0.6	0.3	0.4	0.4	0.2

[a] 2-Amino-3-hydroxynaphthalene. [b] 1,4-Dioxo-3-pyridinium-2-naphthoxide. [c] Not present in the reaction mixture. [d] No attempts have been made to isolate these products quantitatively.

unable to reproduce the reported yield of **8a**. When the reaction was carried out by taking different molar quantities of reactants, the yield at no time was higher than 14% (Experimental Section, Table III). The reaction of equivalent molar quantities of **1** and **2a** in pyridine after detailed chromatographic analysis led to the isolation of **5a** (13%), **6a** (6%), **8a** (10%), and **10a** (0.5%). The reaction of **1** with **2a–d** with or without electron-donating substituents gave similar products in approximately the same yield. But in the case of 2-aminophenols (**2e–h**) having electron-withdrawing substituents, in addition to these products, the heterocyclic quinone **7** was also obtained in good yields, whereas the reaction of **1** with **2i** and **2j** gave only **5**, **7**, and **10**. From these data the reaction of **1** and **2** in pyridine appears to be a complex reaction in which products are obtained by different pathways.

The first and main intermediate in the reaction of **1** and aromatic amines in pyridine is the quaternary pyridinium salt **3** which was already postulated earlier,[13-18] and we were able for the first time[22] to isolate and characterize it by microanalysis, spectroscopic data, and chemical reactions. The assumption that **3** and **5** are intermediates in the formation of **8** was proven by the following experiments. Compound **3** reacts with **2a** in pyridine at 110–130 °C to give **8a** in the same yield as that from the reaction of **1** and **2a**. With the intention of isolating intermediate compounds in the formation of **8a**, we treated **1** and **2a** in 1,2,3-trichloropropane as solvent with 3 equiv of pyridine to give **5a** (X = Cl). The structure of **5a** (X = Cl) was consistent with UV, IR, ^1H NMR, and microanalysis data and with its conversion to the known[17] **5a** (X = ClO_4). Further, **5a** reacts with alkali in the expected manner to give 2-(2-hydroxyphenylimino)-1-oxo-3-pyridinium-4-naphthoxide (**11**) which on treatment with the acid gave the original compound **5a** (X = ClO_4). **5a** was also obtained when **3** and **2a** were reacted in ethanol. When **5a** (X = Cl) was heated in pyridine, it afforded a little 12*H*-benzo[*b*]phenoxazine-6,11-dione (**7a**), starting material, and other intractable matter but no **8a**; so a Smiles-type rearrangement is excluded. However, **5a** in the presence of **2a** under the same conditions yielded **8a** but no **7a**. This suggested to us that **8a** was obtained by a 2-aminophenol exchange reaction. This was confirmed as **5a** with 2-amino-4-chlorophenol (**2e**) in pyridine afforded **8e** and **8a**. Thus **3** and **5** are indeed intermediates in the formation of **8** from **1** and **2**. But it is not certain at which stage in the reaction the pyridine ring of **5** is replaced by hydrogen.

It is well-known[13-18] that in **3** (X = Cl) the chlorine atom is highly reactive due to the pyridinium moiety. When **3** (X = Cl) was reacted with **2a** in acetonitrile under milder conditions (70–80 °C), it afforded **5a** (X = Cl) and **6a** (X = Cl), indicating that initial attack also proceeds by the OH group of **2a** via an intermediate of type **4**. This has been further supported as under the above-mentioned conditions **5a** with **2a** in acetonitrile does not afford **6a** (X = Cl). It has been reported[11,19] that 2-aminophenols in basic medium exist as phenoxide anions, and the latter are more nucleophilic than the amino group. ^{13}C NMR data of a few 2-aminophenols and the corresponding O-methylated derivatives, obtained in different solvents, are listed in Table II. It is clear from these data that the C-1 atoms of 2-aminophenols have considerable difference relative to calculated[23] values in different solvents. The differences cannot be due to solvent effect alone because the analogues O-methylated amines show almost the same values in different solvents. These low-field values of the C-1 atom of **2a** and **2g** in pyridine are toward the side of phenoxide anion, suggesting 2-aminophenols in pyridine may also exist partially as phenoxide anions. The existence of **2** as a phenoxide anion to some extent in pyridine was further supported as under the above-mentioned reaction conditions **1** and **2a** in pyridine gave **5a** and **6a**. The higher yield of the latter in comparison to the reaction of **1** with **2a** in acetonitrile supports our above assumption. From the above data it appears that **3** reacts with the phenoxide anion of **2** to afford an intermediate of type **4**, which on ring closure is transformed to **6**. In practice the corresponding compounds of type **6** have been isolated from the reaction mixture, and their structures were established by microanalysis and spectroscopic properties. It was demonstrated in a separate experiment that under similar conditions **6e** in pyridine afforded little **8e**. This result suggested that **6** is also an intermediate for the formation of **8**. However, the detailed mechanism concerning the

Table II. ^{13}C NMR Chemical Shifts[a] of Aromatic Amines

R^1	R^2	solvent		C-1	C-2
OH	H		calcd[23]	142.1	133.8
OH	H	Me_2SO-d_6	found	143.9	136.4
O	H		calcd	154.8	138.3
O^- + OH	H	pyridine-d_5	found	146.0	138.0
OCH_3	H		calcd	146.6	132.1
OCH_3	H	$CDCl_3$	found[24]	147.3	136.6
OCH_3	H	pyridine-d_5	found	147.5	138.1
OH	NO_2		calcd	147.9	134.7
OH	NO_2	Me_2SO-d_6	found	150.7	137.5
O^-	NO_2		calcd	160.6	139.2
O^- + OH	NO_2	pyridine-d_5	found	152.5	138.8
OCH_3	NO_2		calcd	152.4	133.0
OCH_3	NO_2	pyridine-d_5	found	152.4	139.3

[a] In parts per million relative to $(CH_3)_4Si$.

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source of the hydrogen atom introduced in 8 is still under research. An alternative possibility for the formation of 8 from 10 is ruled out because 10 with pyridine does not afford 8. Indirectly this experiment also supports the idea that 8a could not have been obtained even if A had been used as the starting material by Van Allan and Reynolds.[16]

Compounds 3 and 5 are also found to be intermediates in the formation of 7. The fact that 5a in pyridine slowly afforded minute amounts of 7a gave us the idea that other heterocyclic quinones 7 may be formed from the corresponding 5. To test this assumption 5f was prepared by the reaction of 3 (X = Cl) with 2f in acetonitrile. It was heated with pyridine and gave 7f (87%). The formation of quinones of type 7 is prevailing when 5 has electron-withdrawing substituents in the 2-aminophenol part. Probably when strong electron-withdrawing groups are present in the 2-aminophenol ring of 5, a 2-aminophenol exchange reaction is not preferred; rather elimination of HCl and pyridine is a favorable process and yields the stable heterocyclic quinones 7 in good yields. A 2-aminophenol exchange reaction is a multistep process in which one step is a reversible reaction, and therefore this process is not favorable when strong electron-withdrawing groups are present in 2a. This has been indirectly supported as 5f in pyridine gave a high yield of 7f in comparison to that of 7a obtained from 5a in a similar reaction. The structure of the 12*H*-benzo[*b*]phenoxazine-6,11-diones (7) was proved by microanalysis and UV, IR, ^{1}H NMR, and mass spectra. However, the poor solubility of 7 did not permit a detailed study of which tautomeric form (NH or OH) is predominating. This reaction provides a simple, convenient entry into the new class of heterocyclic quinones 7 which are highly colored and insoluble in common organic solvents.

The formation of chloro-containing phenoxazones (10) can easily be explained by the reaction of unreacted 1 and phenoxide anion to give the intermediate 9 and subsequent ring closure to give 10. There is no chance to isolate the intermediate (9)[11] because under drastic conditions 9 will be rapidly converted to 10. An alternative possibility for the formation of 10 from 3 and 2a or its phenoxide anion was ruled out in a separate experiment; 3 with 2a in pyridine does not yield 10. Another way for the formation of 10 from 1 and 2a via 2-aminophenol exchange reaction is unlikely because 2-aminophenols containing very strong electron-withdrawing groups do not give the phenoxazone.[5,8] The proposed mechanism for the formation of 10 was further strengthened since in no case does the yield of 10 exceed 2%, because most of 1 has already been converted to 3.

UV, IR, and mass spectral data, not already published, of compounds 5a,f, 6a,c,e, 8a–c, 8e–h, and 11 are listed in Table IV (see Supplementary Material).

Experimental Section

Melting points were determined with a Dr. Tottoli apparatus (Büchi) and an aluminum block in open capillaries and are uncorrected. The following instruments were used for spectroscopic analyses: Perkin-Elmer 225 spectrometer (IR), potassium bromide pellets; Gilford 24 (UV/visible); Varian HA-100 and Bruker WH-90 (^{1}H and ^{13}C NMR); Varian CH-7A (mass spectrum, 70 eV). The microanalyses were performed by the Peptide Chemistry Division of the Max Planck Institute of Biochemistry. The purity of the compounds was checked by ascending TLC on Merck precoated silica gel F-254 plates with fluorescent backing and various nonaqueous solvent systems. Spectroscopic data are reported as follows: for ^{1}H NMR spectra, chemical shifts, multiplicity (s = singlet, d = doublet, m = multiplet, mc = multiplet center, br = broad), coupling constants, integration, and assignment; for IR spectra, s = strong, m = medium, w = weak, vs = very strong; for UV spectra, sh = shoulder.

Table III. Reaction of 1 with 2a in Pyridine

amt of reactant			
1 (M)	2a (M)	pyridine (mL)	yields of 8a, %
1×10^{-3}	2×10^{-3}	4	13
1×10^{-3}	2×10^{-3}	3	14
1×10^{-3}	1×10^{-3}	2	10
1×10^{-3}	2×10^{-3}	4	13

General Procedure for the Reaction of 1 with 2-Aminophenol (2a) in Pyridine. 5*H*-Benzo[*a*]phenoxazin-5-one (8a). A mixture of 1 and 2a in dry pyridine was heated at 110–130 °C for 3 h with stirring. After cooling, the suspension was poured into 200 mL of cold water and neutralized with 2 N HCl. It was extracted with chloroform–acetone (1:1), dried over anhydrous sodium sulfate, and column chromatographed (silica gel, 10% H_2O) with benzene as eluent. The second yellow band provided in each case 8a, mp 190 °C. The amount of reactants and yield of 8a are listed in Table III.

Reaction of 1 with 2a in Pyridine. 6-Chloro-5*H*-benzo[*a*]phenoxazin-5-one (10a), 5*H*-Benzo[*a*]phenoxazin-5-one (8a), 2-(2-Hydroxyanilino)-1,4-naphthoquinone-3-pyridinium Perchlorate (5a, X = ClO_4), and 5*H*-Benzo[*a*]phenoxazin-5-one-6-pyridinium Perchlorate (6a, X = ClO_4). A mixture of 1 (2.27 g, 10 mmol) and 2a (1.09 g, 10 mmol) in 25 mL of dry pyridine was heated under reflux for 3 h with stirring. It was cooled to ambient temperature, concentrated, and dried over phosphorus pentoxide under vacuum at room temperature. This crude material was suspended in 1.5 L of water, stirred for 1 h, and filtered. Most of the material was soluble in water, leaving some tarry material. This was triturated with hot chloroform and concentrated. The solution was column chromatographed (alumina grade IV, neutral) and eluted with benzene to give a first pinkish band which was discarded. The second yellow band afforded 15 mg (0.5%) of 10a,[11] mp 203 °C. The next pinkish yellow band gave a crude material containing 8a. It was purified by preparative TLC (silica gel, 2 mm; benzene) to provide 0.24 g (10%) of 8a, identical in every respect with an authentic sample:[20] ^{1}H NMR ($CDCl_3$) δ 8.29 (mc, 1 H, H_1), 8.71 (mc, 1 H, H_4), 7.70–7.88 (m, 3 H, H_2, H_3, H_{11}), 6.43 (s, 1 H, H_6), 7.23–7.51 (m, 3 H, H_8–H_{10}).

To the above water filtrate was added 3 mL of 70% perchloric acid, and after the mixture was cooled, the precipitate was collected by filtration. The filtrate was concentrated to 5 mL, and then 15 mL of ethanol and 50 mL of ether were added. The resulting precipitate gave 2.06 g of crude material. An 18-mg sample of this material was subjected to preparative TLC (silica gel) with methanol as eluent. The second faster moving yellow band afforded 5 mg (13%) of 5a (X = ClO_4), mp 238 °C, identical in all respects (mixture melting point, R_f, and ^{1}H NMR) with the sample prepared by a known method.[17] The shining yellow band at the starting point was extracted with boiling water and provided 2 mg (6%) of a compound suspected to be 6a (X = ClO_4), on the basis of comparison of its R_f value with that of an authentic sample. It was observed that this material decomposes on TLC plates and therefore was not isolated as a pure compound.

Reaction of 1 with 2-Amino-4-methylphenol (2b) in Pyridine. 6-Chloro-10-methyl-5*H*-benzo[*a*]phenoxazin-5-one (10b) and 10-Methyl-5*H*-benzo[*a*]phenoxazin-5-one (8b). A mixture of 1 (2.27 g, 10 mmol) and 2b (1.23 g, 10 mmol) in 20 mL of dry pyridine was heated at 95–120 °C for 2 h with stirring. It was poured into 450 mL of water and the mixture neutralized with concentrated HCl. It was extracted with chloroform–acetone (1:1), dried (Na_2SO_4), and evaporated to dryness to give 0.95 g of crude material. This was column chromatographed (silica gel, 10% H_2O) and eluted with chloroform. The first bluish yellow band of impurities was discarded. Further elution with the same solvent afforded a yellow band to give 14 mg (0.5%) of 10b, mp 229 °C. IR and mass spectra and a mixture melting point proved this material to be identical with that obtained by another method.[11] The column was further eluted with $CHCl_3$–acetone (1:1) to give again a yellow band of unknown substances which was discarded. The next orange-yellow band afforded 0.16 g (5.5%) of 8b[5] as a yellow substance: mp 211–212 °C; ^{1}H NMR ($CDCl_3$) δ 8.30 (mc,

1 H, H_1), 8.72 (mc, 1 H, H_4), 6.43 (s, 1 H, H_6), 7.63–7.81 (m, 3 H, H_2, H_3, H_{11}), 7.23–7.26 (m, 2 H, H_8, H_9), 2.46 (s, 3 H, 10-CH_3).

Reaction of 1 with 2-Amino-3-hydroxynaphthalene (2c) in Pyridine. 5*H*-Dibenzo[*a*,*i*]phenoxazin-5-one-6-pyridinium Perchlorate (6c, X = ClO_4), 6-Chloro-5*H*-dibenzo[*a*,*i*]phenoxazin-5-one (10c), and 5*H*-Dibenzo[*a*,*i*]-phenoxazin-5-one (8c). A mixture of 1 (2.27 g, 10 mmol) and **2c** (1.59 g, 10 mmol) in 20 mL of dry pyridine was heated at 110–130 °C with stirring for 3 h. It was kept overnight in a refrigerator. The orange-red precipitate was collected, washed with a little cold methanol, dried in vacuo (1.6 g), dissolved in 150 mL of hot water, and filtered. Most of the material was soluble in water; to the filtrate was added 2 mL of 70% perchloric acid, and the precipitated compound was filtered off, washed with cold water, and dried. It was purified by crystallization from methanol–ether to yield 1.6 g of orange-red needles of **6c** (X = ClO_4): mp 308 °C; ^1H NMR (Me_2SO-d_6) δ 9.23 (mc, 2 H, H_2', H_6'), 9.02 (mc, 1 H, H_4'), 7.60 (mc, 2 H, H_{10}, H_{11}), 7.98–8.90 (m, 10 H, H_3', H_5', H_1–H_4, H_8, H_9, H_{12}, H_{13}).

Anal. Calcd for $C_{25}H_{15}ClN_2O_6$: C, 63.21; H, 3.18; N, 5.90. Found: C, 63.16; H, 3.37; N, 5.71.

The above pyridine filtrate was poured into 250 mL of ice-cold water, and the suspension was neutralized with concentrated HCl and extracted with a large volume of $CHCl_3$–methanol (1:1). The organic layer afforded 0.5 g of the crude material. This was again suspended in 150 mL of hot water and filtered. Addition of 0.5 mL of 70% perchloric acid to the filtrate gave an additional 0.3 g of **6c** (X = ClO_4), total yield 1.9 g (40%). The material, insoluble in water, was column chromatographed (silica gel, 10% H_2O) with chloroform. First a pinkish yellow band was eluted and rejected. The next yellow band provided 4 mg (0.1%) of **10c** as a yellow substance, mp 282 °C; its properties matched those of an authentic sample.[11] The third yellow pinkish band furnished a mixture of two substances. The yellow substance from the mixture was obtained by preparative TLC (silica gel, 2 mm) using chloroform to yield 8.6 mg (2.6%) of **8c**, mp 288 °C. Recrystallization from chloroform–hexane provided a clean sample of the same melting point: ^1H NMR ($CDCl_3$) δ 8.76 (mc, 1 H, H_4), 6.5 (s, 1 H, H_6), 8.24–8.42 (m, 2 H, H_1, H_{13}), 7.28–8.04 (m, 7 H, H_2, H_3, H_8–H_{12}).

Anal. Calcd for $C_{20}H_{11}NO_2$: C, 80.78; H, 3.73; N, 4.71. Found: C, 80.30; H, 3.70; N, 4.63.

Reaction of 1 with 3-Amino-4-hydroxybenzoic Acid (2d) in Pyridine. 10-Carboxy-6-chloro-5*H*-benzo[*a*]phenoxazin-5-one (10d), 10-Carboxy-5*H*-benzo[*a*]phenoxazin-5-one (8d), and 1,4-Dioxo-3-pyridinium-2-naphthoxide. A mixture of 1 (2.27 g, 10 mmol) and **2d** (1.53 g, 10 mmol) in 20 mL of dry pyridine was heated at 90–130 °C with stirring for 5 h. It was put into the refrigerator for 12 h. The precipitate was isolated by filtration, washed with a little methanol, and dried to give 1.0 g of crude material. This was dissolved in a minimum amount of dichloromethane–methanol (1:1), column chromatographed (silica gel, 10% H_2O), and eluted with acetone. The first yellow band, containing little substance, was discarded. The second yellow band provided 1,4-dioxo-3-pyridinium-2-naphthoxide: 0.40 g (16%); mp 305 °C (confirmed by comparison of IR and ^1H NMR with those of the authentic sample[14]). The above pyridine filtrate was poured into 250 mL of cold water and neutralized with concentrated HCl. The precipitate was collected, washed with 500 mL of cold water, and dried to yield 2.2 g of crude material. This was extracted with dichloromethane–acetone and column chromatographed (silica gel, 10% H_2O) with acetone. A yellow band of a complex mixture was eluted and rejected. Then the column was run with acetone–methanol (9:1) to give again a yellow band, which on evaporation gave 0.123 g of substance. The mass spectrum indicated that it was a mixture of **8d** (mol wt 291) and **10d** (mol wt 325/327). Separation of the phenoxazones could not be achieved by TLC using different solvent systems.

Reaction of 1 with 2-Amino-4-chlorophenol (2e) in Pyridine. 10-Chloro-5*H*-benzo[*a*]phenoxazin-5-one-6-pyridinium Perchlorate (6e), 6,10-Dichloro-5*H*-benzo[*a*]phenoxazin-5-one (10e), 10-Chloro-5*H*-benzo[*a*]phenoxazin-5-one (8e), and 2-Chloro-12*H*-benzo[*b*]phenoxazine-6,11-dione (7e). A mixture of 1 (2.27 g, 10 mmol) and **2e** (1.43 g, 10 mmol) in 20 mL of dry pyridine was heated at 90–130 °C with stirring for 3 h. It was cooled to ambient temperature, and the solvent was removed; the residue was dried over P_2O_5 to give a dirty colored substance. This was extracted with 200 mL of cold water and filtered. To the filtrate was added 0.5 mL of 70% perchloric acid, and the precipitate was isolated, washed with 750 mL of cold water, and dried in vacuo to yield 150 mg of **6e**. The above crude material was again treated with 1.5 L of warm water (40–50 °C) and filtered, and an additional 310 mg of **6e** was obtained from this filtrate (total yield 460 mg, 9%). Several recrystallizations from acetonitrile–ether afforded an analytical sample of **6e** (X = ClO_4) as light shining greenish yellow plates: mp 334 °C; ^1H NMR (Me_2SO-d_6) 9.1–9.2 (m, 2 H, H_2', H_6'), 7.63 (mc, 2 H, H_8, H_9), 8.5–8.91 (m, 2 H, H_4, H_4'), 8.12–8.51 (m, 6 H, H_1–H_3, H_{11}, H_3', H_5').

Anal. Calcd for $C_{21}H_{12}Cl_2N_2O_6$: C, 54.90; H, 2.63; N, 6.10. Found: C, 54.50; H, 2.69; N, 6.25.

The water-insoluble material was filtered over silica gel (10% H_2O) with chloroform–acetone (1:3) to give a mixture of **8e**, **10e**, **7e**, and other colored materials, leaving much polar compound on the column. The mixture was suspended in 200 mL of hot chloroform and filtered. This gave a small portion of undissolved substance, which was washed with 100 mL of cold methanol to yield 45 mg (1.5%) of **7e**. An analytical sample of **7e** was obtained by washing it with a large volume of cold methanol–$CHCl_3$ (2:1) as shining blue crystals: mp >300 °C; UV (Me_2SO) λ_{max} nm (log ϵ) 304 (4.21), 555.5 (sh, 2.68); IR (KBr) 3334 (v), 3050 (w), 1640 (vs), 1585 (s), 1570 (m), 870 (m), 825 (s), 779 (m), 770 cm^{-1}; ^1H NMR (Me_2SO-d_6) δ 8.91 (s, 1 H, NH), 6.78 (d, J = 2 Hz, 1 H, H_1), 6.69–6.7 (m, 2 H, H_3, H_4), 7.75–7.97 (m, 4 H, H_7–H_{10}); mass spectrum, m/e (relative intensity) 297 (M^+, 100), 269 (17), 253 (6), 241 (8), 234 (21), 213 (11), 206 (17), 190 (8), 186 (7), 178 (39), 177 (21), 152 (7), 151 (36), 150 (22), 149 (6), 132 (7), 110 (9), 105 (40), 104 (10), 102 (7).

Anal. Calcd for $C_{16}H_8ClNO_3$: C, 64.54; H, 2.71; N, 4.70. Found: C, 64.64; H, 2.39; N, 4.36. The above filtrate was column chromatographed (silica gel, 10% H_2O) and eluted with $CHCl_3$. A first yellow band was discarded. On further elution the next yellow band afforded 65 mg (2%) of **10e**, mp 236 °C; it was confirmed by comparison of its spectral properties with those of an authentic sample.[11] The third band on evaporation yielded 0.195 g (7%) of yellow crystals of **8e**: mp 236–237 °C; ^1H NMR ($CDCl_3$) δ 8.70 (mc, 1 H, H_4), 6.45 (s, 1 H, H_6), 8.30 (mc, 1 H, H_1), 7.30–7.50 (m, 2 H, H_8, H_9), 7.73–7.84 (m, 3 H, H_2, H_3, H_{11}).

General Procedure for the Reaction of 1 with 2f–h in Pyridine. Substituted 12*H*-Benzo[*b*]phenoxazine-6,11-dione (7), Substituted 6-Chloro-5*H*-benzo[*a*]phenoxazin-5-one (10), and Substituted 5*H*-Benzo[*a*]phenoxazin-5-one (8). A mixture of 1 (2.27 g, 10 mmol) and substituted **2** (10 mmol) in 20 or 25 mL of dry pyridine was heated at 130–140 °C with stirring for 2–3 h. The reaction solution was then allowed to stand at −2 °C for 12 h. The precipitate was collected, washed with hot water and methanol, and dried to give the corresponding **7**. The clean product **7** was obtained by washing it with 500 mL of hot methanol or by crystallization with pyridine.

The above pyridine filtrate was poured into 300 mL of ice-cold water and neutralized with concentrated HCl. The suspension was extracted three times with $CHCl_3$–acetone (1:1), the organic phase was dried over anhydrous sodium sulfate and concentrated in vacuo to give crude material. This was dissolved in a minimum amount of acetone and applied on several TLC plates (silica gel, 0.5 mm) with benzene as the developing system. The first dark yellow band in each case afforded the corresponding substituted 6-chloro-5*H*-benzo[*a*]phenoxazin-5-one (**10**). The next yellow band furnished the corresponding substituted 5*H*-benzo[*a*]phenoxazin-5-one (**8**). The structures of all the phenoxazones were confirmed by comparison (mixture melting point, IR and mass spectra) with those of the corresponding phenoxazones synthesized by known methods.

Reaction of 1 with 2-Amino-4,6-dichlorophenol (2f) in Pyridine. 2,4-Dichloro-12*H*-benzo[*b*]phenoxazine-6,11-dione (7f), 6,8,10-Trichloro-5*H*-benzo[*a*]phenoxazin-5-one (10f), and 8,10-Dichloro-5*H*-benzo[*a*]phenoxazin-5-one (8f). The reaction of 1 with **2f** in pyridine as described above provides 1.01 g (33%) of **7f** as blue leaflets: mp >300 °C; UV (dioxane) λ_{max} nm (log ϵ) 234.5 (4.35), 306 (4.41), 573 (3.00); IR (KBr) 3470 (w), 3337 (vs), 2960 (w), 1665 (vs), 1640 (vs), 1586 (s), 1571 (s), 886 (w), 850 (s), 755 (m), 717 (s) cm^{-1}; ^1H NMR (Me_2SO-d_6) δ 9.11 (s, 1 H, NH or OH), 6.94 (d, J_m = 2 Hz, H_1), 6.76 (d, J_m = 2 Hz,

1 H, H_3), 7.83–7.89 (m, 4 H, H_7–H_{10}); mass spectrum, *m/e* (relative intensity) 333 (69), 331 (M^+, 100), 300 (11), 275 (5), 268 (18), 247 (4), 240 (8), 212 (12), 211 (6), 177 (19), 166 (5) 150 (8), 138 (6), 106 (10), 105 (25), 104 (37).

Anal. Calcd for $C_{16}H_7Cl_2NO_3$: C, 57.85; H, 2.13; N, 4.22. Found: C, 57.81; H, 2.05; N, 4.08.

A 23-mg (0.6%) amount of **10f**[11] (mp 263 °C) was also obtained as well as 0.3 g (0.9%) of **8f**:[5] mp 221 °C; ^1H NMR ($CDCl_3$) δ 8.68 (mc, 1 H, H_4), 8.30 (mc, 1 H, H_1), 6.55 (s, 1 H, H_6), 7.51 (d, $J_{9,11}$ = 2.35 Hz, 1 H, H_9), 7.73 (d, $J_{9,11}$ = 2.35 Hz, 1 H, H_{11}), 7.78–7.85 (m, 2 H, H_2, H_3).

Reaction of 1 with 2-Amino-4-nitrophenol (2g) in Pyridine. 2-Nitro-12*H*-benzo[*b*]phenoxazine-6,11-dione (7g), 6-Chloro-10-nitro-5*H*-benzo[*a*]phenoxazin-5-one (10g), and 10-Nitro-5*H*-benzo[*a*]phenoxazin-5-one (8g). The reaction of **1** and **2g** in pyridine gave 1.45 g (47%) of **7g** as shining blue needles, crystallized from pyridine: mp >300 °C; UV (Me_2SO) λ_{max} nm (log ε) 305 (4.42), 437 (3.62), 559 (2.50); IR (KBr) 3328 (vs), 3094 (w), 3057 (w), 1640 (vs), 1617 (vs), 1596 (s), 1577 (m), 1520 (vs), 1338 (s), 879 (s), 817 (s), 740 (s), 715 (vs) cm^{-1}; mass spectrum, *m/e* (relative intensity) 308 (M^+, 100), 278 (4), 263 (15), 262 (81), 250 (10), 234 (14), 206 (11), 178 (16), 154 (5), 152 (4), 151 (18), 131 (6), 129 (5), 105 (8), 104 (22), 102 (5).

Anal. Calcd for $C_{16}H_8N_2O_5$: C, 62.34; H, 2.61; N, 9.09. Found: C. 62.62; H, 2.60; N, 9.32.

A 12-mg (0.3%) amount of **10g**[11] (mp 291 °C) was obtained as well as 50 mg (1.7%) of **8g**:[21] mp 246–247 °C; ^1H NMR ($CDCl_3$) δ 8.70–8.8 (m, 2 H, H_4, H_{11}), 6.52 (s, 1 H, H_6), 7.44 (d, $J_{8,9}$ = 9 Hz, 1 H, H_8), 7.78–7.88 (m, 2 H, H_2, H_3), 8.25–8.44 (m, 2 H, H_1, H_9).

Reaction of 1 with 2-Amino-5-nitrophenol (2h) in Pyridine. 3-Nitro-12*H*-benzo[*b*]phenoxazine-6,11-dione (7h), 6-Chloro-9-nitro-5*H*-benzo[*a*]phenoxazin-5-one (10h), and 9-Nitro-5*H*-benzo[*a*]phenoxazin-5-one (8h). The reaction of **1** with **2h** in pyridine afforded 2.02 g (65.5%) of **7h** as shining needles which were crystallized from pyridine: mp >300 °C; UV (Me_2SO) λ_{max} nm (log ε) 306 (4.44), 4405 (3.38), 642 (2.07); IR (KBr) 3328 (vs), 3092 (w), 3064 (w), 1640 (vs), 1616 (s), 1585 (s), 1571 (s), 1518 (vs), 1338 (s), 878 (s), 816 (s), 740 (s), 715 (vs) cm^{-1}.

Anal. Calcd for $C_{16}H_8N_2O_5$: C, 62.34; H, 2.61; N, 9.09. Found: C, 62.43; H, 2.87; N, 8.85.

A 12-mg (0.4%) amount of **10h**[11] (mp 248 °C) was also obtained as well as 38 mg (1.3%) of **8h**:[5] mp 264–265 °C; ^1H NMR ($CDCl_3$) δ 8.72 (mc, 1 H, H_4), 6.51 (s, 1 H, H_6), 8.01 (mc, 1 H, H_{11}), 7.71–7.91 (m, 2 H, H_2, H_3), 8.15–8.35 (m, 3 H, H_1, H_8, H_{10}).

Reaction of 1 with 3-Acetyl-2-aminophenol (2i) in Pyridine. 1-Acetyl-12*H*-benzo[*b*]phenoxazine-6,11-dione (7i) and 11-Acetyl-6-chloro-5*H*-benzo[*a*]phenoxazin-5-one (10i). A mixture of **1** (2.27 g, 10 mmol) and **2i** (1.51 g, 10 mmol) in 20 mL of dry pyridine was heated at 120–130 °C with stirring for 3 h. It was chilled overnight in a refrigerator, and the precipitate was collected, washed with 100 mL of methanol, and dried to give 1.4 g of **7i**, mp 258 °C. Recrystallization with dichloromethane–hexane furnished an analytical sample: UV (Me_2SO) λ_{max} nm (log ε) 306.5 (4.23), 440.5 (3.70); IR (KBr) 3290 (vs), 3060 (w), 1660 (vs), 1645 (vs), 1589 (m), 1570 (s), 1462 (s), 779 (s), 709 (vs) cm^{-1}; ^1H NMR (Me_3SO-d_6) δ 9.61 (s, 1 H, NH), 2.56 (s, 3 H, CH_3 of acetyl), 7.46 (s, 1 H, H_2), 6.8–6.98 (m, 2 H, H_3, H_4), 7.80–7.91 (m, 4 H, H_7–H_{10}); mass spectrum, *m/e* (relative intensity) 305 (M^+, 100), 290 (27), 288 (8), 287 (36), 263 (8), 262 (31), 259 (14), 234 (18), 231 (5), 205 (8), 203 (11), 202 (8), 178 (6), 177 (11), 152 (6), 151 (20), 150 (8), 129 (4), 105 (8), 104 (13), 102 (8), 101 (11).

Anal. Calcd for $C_{18}H_{11}NO_4$: C, 70.80; H, 3.63; N, 4.59. Found: C, 70.90; H, 3.85; N, 4.58.

The above pyridine filtrate was diluted with water to 200 mL, neutralized with concentrated HCl and extracted with chloroform–acetone (1:1). The organic layer was dried over Na_2SO_4, concentrated, and purified by preparative TLC (silica gel, 2 mm), being developed four times with benzene. It yielded another 45 mg of **7i** (total yield 1.45 g, 47%) and 15 mg (0.4%) of yellow **10i** (mp 253 °C), identical by IR, mixture melting point, and mass spectrum with a sample of known orientation.[11]

Reaction of 1 with 2-Amino-3,4,6-trichlorophenol (2j) in Pyridine. 1,2,4-Trichloro-12*H*-benzo[*b*]phenoxazine-6,11-dione (7j) and 6,8,10,11-Tetrachloro-5*H*-benzo[*a*]phenoxazine-5-one (10j). A mixture of **1** (2.27 g, 10 mmol) and **2j** (2.01 g, 10 mmol) in 25 mL of dry pyridine was heated under reflux for 3 h with stirring. The mixture, which had turned from dark yellow to dark bluish green, was allowed to cool at ambient temperature, and 20 mL of methanol was added. The solid was collected by filtration, washed with 100 mL of methanol, and dried to give 3 g of **7j**, mp 280 °C. A pure sample of the same melting point was obtained by recrystallization with dichloromethane–hexane: UV (Me_2SO) λ_{max} nm (log ε) 307 (4.33), 583.5 (4.04), 642 (2.04); IR (KBr) 3395 (w), 3375 (s), 3090 (w), 1657 (vs), 1583 (s), 1561 (w), 880 (m), 840 (m), 788 (m), 778 (m) cm^{-1}; ^1H NMR (Me_2SO-d_6) δ 7.14 (s, 1 H, NH or OH), 7.32 (s, 1 H, H_1), 7.86–7.93 (m, 4 H, H_7–H_{10}); mass spectrum, *m/e* (relative intensity) 365 (M^+, 100), 339 (16), 338 (4), 337 (16), 330 (6), 311 (7), 309 (8), 304 (15), 303 (5), 302 (23), 283 (6), 281 (7), 276 (10), 274 (15), 248 (13), 247 (9), 246 (21), 245 (6), 213 (12), 212 (8), 211 (39), 210 (8), 184 (5), 178 (7), 176 (11), 175 (16), 149 (11), 148 (15), 133 (4), 132 (4), 105 (45), 104 (50).

Anal. Calcd for $C_{16}H_6Cl_3NO_3$: C, 52.37; H, 1.65; N, 3.82; Cl, 29.09. Found: C, 52.56; H, 1.67; N, 3.89; Cl, 29.40.

The above filtrate was poured into 200 mL of ice-cold water and neutralized with concentrated HCl. The precipitate was isolated by extraction with chloroform–acetone (2:1) to give 0.425 g of crude material. This was column chromatographed over silica gel (10% H_2O) with benzene as eluent. The first faster moving band was rejected. The next dirty yellow band after preparative TLC (silica gel, 2 mm; benzene; three times) afforded 0.01 g (0.2%) of **10j**, mp 302 °C; its spectral properties are identical with those of a known sample.[11] The next blue band afforded an additional 0.33 g of **7j**, total yield 3.3 g (92%).

2-(2-Hydroxyanilino)-1,4-naphthoquinone-3-pyridinium Chloride (5a, X = Cl). A mixture of **1** (2.27 g, 10 mmol) and dry pyridine (2.37 g, 30 mmol) was heated at 50–60 °C in 1,2,3-trichloropropane for 0.5 h. Then 2-aminophenol (**2a**; 1.09 g, 10 mmol) was added to the above suspension. The mixture was heated to 80–90 °C for 2 h. The suspension was then kept in a refrigerator for 12 h. The precipitate was isolated by filtration, washed with a little methanol–water (5:1) and hexane, and dried in vacuo to give 1.6 g (42%) of **5a** (X = Cl). Two crystallizations from dry methanol–ether afforded an analytical sample as yellow crystals. It starts to become black at 240 °C and melts at 296–300 °C. It was highly hygroscopic, and for analysis it was dried in vacuo over P_2O_5 at 90–100 °C for 1 week: ^1H NMR (MeOH-d_4) δ 9.0 (mc, 2 H, H_2', H_6'), 8.83 (mc, 1 H, H_4'), 7.17–7.44 (m, 4 H, H_2–H_5, anilino), 7.7–8.5 (m, 6 H, H_5–H_8, H_3', H_5').

Anal. Calcd for $C_{21}H_{15}ClN_2O_3 \cdot {}^1/_3H_2O$: C, 65.52; H, 4.10; N, 7.28. Found: C, 65.45; H, 4.45; N, 7.22.

2-(2-Hydroxyanilino)-1,4-naphthoquinone-3-pyridinium Perchlorate (5a, X = ClO_4). Method A. To a 20-mL solution of **5a** (X = Cl; 0.2 g, 0.5 mmol) in water was added 0.1 mL of 70% perchloric acid. The resulting precipitate was isolated by filtration, washed with cold water, and dried. Crystallization with methanol–ether afforded 0.12 g (51%) of clean **5a** (X = ClO_4), mp 238 °C.

Method B. To a 0.0342-g (0.1 mmol) suspension of **11** in 4 mL of water was added 0.2 mL of 70% perchloric acid. The resulting suspension was stirred for 1 h at room temperature. The yellow precipitate was collected by filtration, washed with cold water, and dried in vacuo to give 0.03 g (68%) of **5a** (X = ClO_4), mp 238 °C.

Method C. A mixture of **3** (X = ClO_4; 0.37 g, 1 mmol) and **2a** (0.109 g, 1 mmol) in 7 mL of ethanol was heated at 70–80 °C with stirring for 3 h. It was cooled, and the product was isolated, washed with a little dilute methanol, and dried to yield 350 mg of crude material, which was purified by preparative TLC (silica gel, 0.5 mm) with methanol as eluent. The faster moving band furnished 250 mg (56%) of **5a**. It was further purified by crystallization with methanol–ether; mp 238 °C. The mixture melting point, R_f, and ^1H NMR spectra of the materials synthesized by methods A, B, and C were identical in every respect with the authentic sample of **5a** (X = ClO_4):[17] ^1H NMR (Me_2SO-d_6) δ 9.08 (mc, 2 H, H_2', H_6'), 8.85 (mc, 1 H, H_4'), 10.94 (br, 2 H, NH, OH, D_2O exchangeable), 7.0–8.21 (m, 6 H, H_5–H_8,H_3', H_5').

2-(2-Hydroxyphenylimino)-1-oxo-3-pyridinium-4-naphthoxide (11). To a stirred solution of 0.36 g (1 mmol) of **5a** (X = Cl) in 20 mL of hot water was added 10 mL of a saturated solution of sodium carbonate. The mixture was warmed on a water bath for 5 min and stirred at ambient temperature for 1 h. The

precipitate was collected, washed with water, and dried to give 0.22 g (65%) of a brick-red substance. Repeated recrystallization from dry methanol–chloroform provided an analytical sample of 11. It starts to blacken at 198 °C and melts at 243–245 °C. For analysis and spectroscopic investigation it was dried under vacuum at 80 °C over P_2O_5 for 3 days: ^1H NMR (Me_2SO-d_6) δ 8.89 (mc, 2 H, H_2', H_6'), 8.55 (mc, 1 H, H_4') 7.51–8.20 (m, 6 H, H_5–H_8, H_3', H_5'), 7.15–7.92 (m, 4 H, H_2–H_5 anilino protons).

Anal. Calcd for $C_{21}H_{14}N_2O_3$: C, 73.66; H, 4.12; N, 8.18. Found: C, 73.14; H, 4.07; N, 8.25.

Reaction of 5a (X = Cl) with Pyridine. 12*H*-Benzo[*b*]phenoxazine-6,11-dione (7a). A mixture of **5a** (X = Cl; 8 mg, 2.1×10^{-5} mol) in 1 mL of dry pyridine was heated at 95–100 °C for 3 h. It was cooled to ambient temperature and poured into 20 mL of ice-cold water, neutralized with HCl, and extracted with chloroform–acetone (1:1). The organic phase was dried over anhydrous sodium sulfate. The extract was evaporated to dryness, and subjected to TLC (acetone); it showed the presence of starting material, a blue compound, and other intractable material. The mixture was dissolved in acetone and subjected to preparative TLC with acetone as eluent to give the following compounds. The first blue band yielded the 0.5 mg (9%) of **7a**[12] on the basis of its mass spectrum: *m/e* (relative intensity) 263 (M^+, 100), 235 (18), 207 (9), 206 (6), 180 (6), 179 (22), 178 (13), 152 (16), 151 (12), 105 (23), 104 (30). The second yellow band gave the 3 mg of **5a** (X = Cl; mp 292–300 °C dec) which was identical in every respect with the starting material.

Reaction of 5a (X = Cl) with 2-Amino-4-chlorophenol (2e) in Pyridine. 10-Chloro-5*H*-benzo[*a*]phenoxazin-5-one (8e) and 5*H*-Benzo[*a*]phenoxazin-5-one (8a). A mixture of **5a** (X = Cl; 33 mg, 8.7×10^{-5} mol) and **2e** (15 mg, 1.0×10^{-4} mol) in 2 mL of dry pyridine was heated at 130–140 °C for 3 h. It was diluted with water to 20 mL, neutralized with concentrated HCl and extracted with chloroform–acetone (1:1). The organic phase was evaporated to dryness, dissolved in a minimum amount of acetone, applied to TLC plates (silica gel, 2 mm), and developed by using benzene as the solvent system (five times). The first yellow band afforded 1.8 mg (9%) of **8e**, mp 236–237 °C. The second band gave 0.8 mg (3%) of **8a**, mp 190 °C. The structures of the phenoxazones were established by comparing them with known orientation samples[5,20] (melting point, mass spectrum, and R_f value).

In a separate experiment the above reaction at 80–90 °C for 1 h showed only the presence of starting materials and not the phenoxazones.

Reaction of 3 (X = Cl) with 2a in Acetonitrile. 2-(2-Hydroxyanilino)-1,4-naphthoquinone-3-pyridinium Chloride (5a, X = ClO_4) and 5*H*-Benzo[*a*]phenoxazin-5-one-6-pyridinium Chloride (6a, X = Cl). A mixture of **3** (X = Cl;[22] 0.152 g, 0.5 mmol) and **2a** (0.082 g, 0.75 mmol) in 4 mL of acetonitrile was heated at 50–70 °C for 2.5 h with stirring. The resulting suspension was chilled and filtered, and the precipitate was dried in vacuo. This was boiled with 250 mL of ethyl acetate and filtered to remove excess of **2a** and other impurities. Then it was applied to TLC plates (silica gel, 2 mm) and developed by using methanol as the eluent. The first yellow band afforded 94 mg (50%) of **5a** (X = Cl, mp 296–300 °C dec) and had the same spectral data as a sample prepared by another method. The second shining yellow band at the starting point seems to be **6a** (X = Cl) on the basis of its R_f value. The approximate yield was calculated from the rest of substance remaining on the TLC plates; 10 mg (6%). This could not be isolated in pure form from the TLC plates because it decomposes.

Reaction of 2-Chloro-1,4-naphthoquinone-3-pyridinium Chloride (3, X = Cl) with 2-Aminophenol (2a) in Pyridine under Milder Conditions. 5*H*-Benzo[*a*]phenoxazin-5-one-6-pyridinium Perchlorate (6a, X = ClO_4). A suspension of **2a** (0.109 g, 1 mmol) in 3 mL of dry pyridine was heated at 70–80 °C for 30 min, and then **3** (X = Cl;[22] 0.305 g, 1 mmol) was added. The suspension was heated at 80–90 °C for 1 h and cooled. The solvent was evaporated in vacuo, and the crude material was dried under vacuum over P_2O_5. It was suspended in 150 mL of cold water and filtered. To the filtrate was added 0.5 mL of 70% perchloric acid. The resulting light yellow precipitate was collected, washed with cold water, and dried to give 0.1 g (24%) of **6a** (X = ClO_4). Two crystallizations from acetonitrile–ether provided a pure sample as a yellow powder. It starts to change color at 170 °C and melts at 265–270 °C: ^1H NMR (Me_2SO-d_6) δ 9.15 (mc, 2 H, H_2', H_6'), 8.68 (mc, 1 H, H_4'), 7.44–8.51 (m, 10 H, H_1–H_4, H_7–H_{10}, H_3', H_5').

Anal. Calcd for $C_{21}H_{13}ClN_2O_6$: C, 59.36; H, 3.08; N, 6.59. Found: C, 58.72; H, 3.19; N, 6.85.

2-(3,5-Dichloro-2-hydroxyanilino)-1,4-naphthoquinone-3-pyridinium Chloride (5f, X = Cl). A mixture of **3** (X = Cl)[22] (0.306 g, 1 mmol) and 2-amino-4,6-dichlorophenol (**2f**; 0.178 g, 1 mmol) in 7 mL of acetonitrile was heated at 70–90 °C for 2 h with stirring. The reaction mixture was chilled, filtered, washed with ether, and dried. It was applied on TLC plates (silica gel, 2 mm) and developed with methanol. The second faster moving yellow band provided 0.21 g (47%) of **5f** (X = Cl). An analytical sample of **5f** as a yellow powder was obtained by several crystallizations with methanol–ether. It starts to change color at 170 °C and has an uncertain melting point: ^1H NMR (Me_2SO-d_6) δ 8.90 (mc, 2 H, H_2', H_6'), 8.57 (mc, 1 H, H_4'), 7.4–8.21 (m, 6 H, H_5–H_8, H_3', H_5'), 7.10 (d, J = 2.5 Hz, 1 H, H_4, anilino ring), 6.87 (d, J = 2.5 Hz, 1 H, H_6, anilino ring), 7.4–7.8 (br, 2 H, NH, OH, D_2O exchangeable).

Anal. Calcd for $C_{21}H_{13}Cl_3N_2O_2$: C, 56.33; H, 2.92; N, 6.25. Found: C, 57.16; H, 2.87; N, 6.26.

Reaction of 2-(3,5-Dichloro-2-hydroxyanilino)-1,4-naphthoquinone-3-pyridinium Chloride (5f, X = Cl) in Pyridine. 2,4-Dichloro-12*H*-benzo[*b*]phenoxazine-6,11-dione (7f). A mixture of **5f** (X = Cl) (15 mg, 3.3×10^{-1} mol) in 0.2 mL of dry pyridine was heated at 120–140 °C for 2 h. The suspension was evaporated to dryness in vacuo and then washed well with hot methanol to give 6 mg (81%) of blue leaflets (mp >300 °C) identical in every respect with a sample prepared by another method.

Registry No. **1**, 117-80-6; **2a**, 95-55-6; **2b**, 95-84-1; **2c**, 5417-63-0; **2d**, 1571-72-8; **2e**, 95-85-2; **2f**, 527-62-8; **2g**, 99-57-0; **2h**, 121-88-0; **2i**, 4502-10-7; **2j**, 6358-15-2; **3** (X = ClO_4), 75112-53-7; **3** (X = Cl), 74292-48-1; **5a** (X = ClO_4), 1252-75-1; **5a** (X = Cl), 75197-75-0; **5f** (X = Cl), 75197-76-1; **6a** (X = ClO_4), 75197-78-3; **6a** (X = Cl), 75197-79-4; **6c** (X = ClO_4), 75197-81-8; **6e** (X = ClO_4), 75197-83-0; **7a**, 75197-84-1; **7e**, 75197-85-2; **7f**, 75197-86-3; **7g**, 75197-87-4; **7h**, 75197-88-5; **7i**, 75213-90-0; **7j**, 75197-89-6; **8a**, 1924-19-2; **8b**, 1924-20-5; **8c**, 2219-04-7; **8d**, 75197-90-9; **8e**, 75197-91-0; **8f**, 75213-91-1; **8g**, 75197-92-1; **8h**, 75197-93-2; **10a**, 73397-07-6; **10b**, 73397-08-7; **10c**, 75197-94-3; **10d**, 73397-16-7; **10e**, 73397-09-8; **10f**, 73397-13-4; **10g**, 73397-11-2; **10h**, 73397-12-3; **10i**, 73397-15-6; **10j**, 73397-14-5; **11**, 75197-95-4; 1,4-dioxo-3-pyridinium-2-naphthoxide, 21758-86-1.

Supplementary Material Available: UV, IR, and mass spectral data of compounds **5a,f**, **6a,c,e**, **8a–c**, **8e–h**, and **11** (1 page). Ordering information is given on any current masthead page.