# *Cine*-substitution in reactions of dichloro-1,4-benzoquinones with pyrrolidine

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Products of *cine*-substitution are formed in reactions of 2,5- and 2,6-dichloro-1,4-benzoquinones with pyrrolidine. The main reason for amination of chloroquinones by pyrrolidine *via* the mechanism of *cine*-substitution is the high basicity of this amine. A high degree of localization of the π-bond in the molecules of the starting chloroquinones and the strong conjugation of the amino group with the quinone ring in the molecules of the intermediate monoaminoquinones are two other factors that favor an increase in yields of the products of *cine*-substitution.

**Key words:** chloroquinones, aminoquinones, nucleophilic substitution.

Reactions of chloroquinones with amines have been the subject of detailed studies for many years, which is reflected in the many works devoted both to the synthetic use and to the study of the mechanism of these reactions.[1,2] Depending on the structure of chloroquinones, their amination can involve either reductive addition of amines of quinones or nucleophilic substitution of the chlorine atoms in the quinone ring by amines. All reactions of nucleophilic substitution of chloroquinones described[1,2] indicate that the replacement of chlorine atoms by amino groups in molecules of these compounds proceed exclusively *via* the $S_N2Ar$ mechanism. The most convincing confirmation of this mechanism comes from studying the reactions of 2,5-dichloro-1,4-benzoquinone (**1**) and its 2,6-dichloro-isomer with amines. It has been shown[3] that the sole products of the amination of the latter by amines are the corresponding 2,5-bis(amino)-3-chloro-1,4-benzoquinones. Similarly, quinone **1** reacts with amines to give only two types of final bisaminated products.[3–5] The main direction of the reactions is the consecutive reductive addition of two amine molecules at positions 3 and 6 of quinone **1** resulting in the formation of 2,5-bis(amino)-3,6-dichloro-1,4-benzoquinones. At the same time, the nucleophilic replacement of both chlorine atoms by amino groups in a molecule of compound **1** gave 2,5-bis(amino)-1,4-benzoquinones as minor products.[3,5]

It is shown in this work that one of the main directions of the reactions of dichloroquinone **1** (Scheme 1) and 2,6-dichloro-1,4-benzoquinone (**9**) (Scheme 2) with pyrrolidine is the *cine*-substitution (mechanism $AE_a$)[6] of amino groups for chlorine atoms in molecules of the initial chloroquinones or in the products of their intermediate amination. As a result, the main product of the reaction of quinone **1** with pyrrolidine is 2,5-bis(pyrrolidino)-3-chloro-1,4-benzoquinone (**8**), and the amination of quinone **9** by pyrrolidine gives 2,5-bis(pyrrolidino)-1,4-benzoquinone (**6**) along with bisaminoquinone **8**, which was theoretically expected.

The addition of excess pyrrolidine to quinone **1** in THF at room temperature resulted unexpectedly in the formation of three products, which, according to the data of elemental analysis and spectral studies, corresponded to bisaminoquinones **6**, **7**, and **8**. Based on the published analogies,[1–5] one may assume that the formation of aminoquinone **6** in this reaction is caused by the nucleophilic replacement of two chlorine atoms by pyrrolidine in compound **1** (Scheme 1). Aminoquinone **7** is formed due to the consecutive reductive addition of two pyrrolidine molecules at positions 3 and 6 of the initial quinone **1**. The unexpected formation of aminoquinone **8** as the main product, obtained in 36% yield, indicates that the reaction includes one more, previously unknown direction of amination of quinone **1**. Moreover, in the case of pyrrolidine, it is precisely this direction that becomes the main one. A change in the reaction conditions (boiling in THF or MeOH) virtually did not change the ratio of aminoquinones **6**, **7**, and **8** formed in the reaction. In all cases, the main product of the reaction was aminoquinone **8**, whose yield was 34—36%.

An interesting peculiarity of the $^1H$ NMR spectrum of compound **8** is the substantial difference in the spectral parameters of the protons of the $NCH_2$ groups of its two pyrrolidine fragments. For example, the protons of the $NCH_2$ group of the pyrrolidine fragment in position 5 of the quinone ring of compound **8** appear as two strongly broadened singlets of the same intensity at

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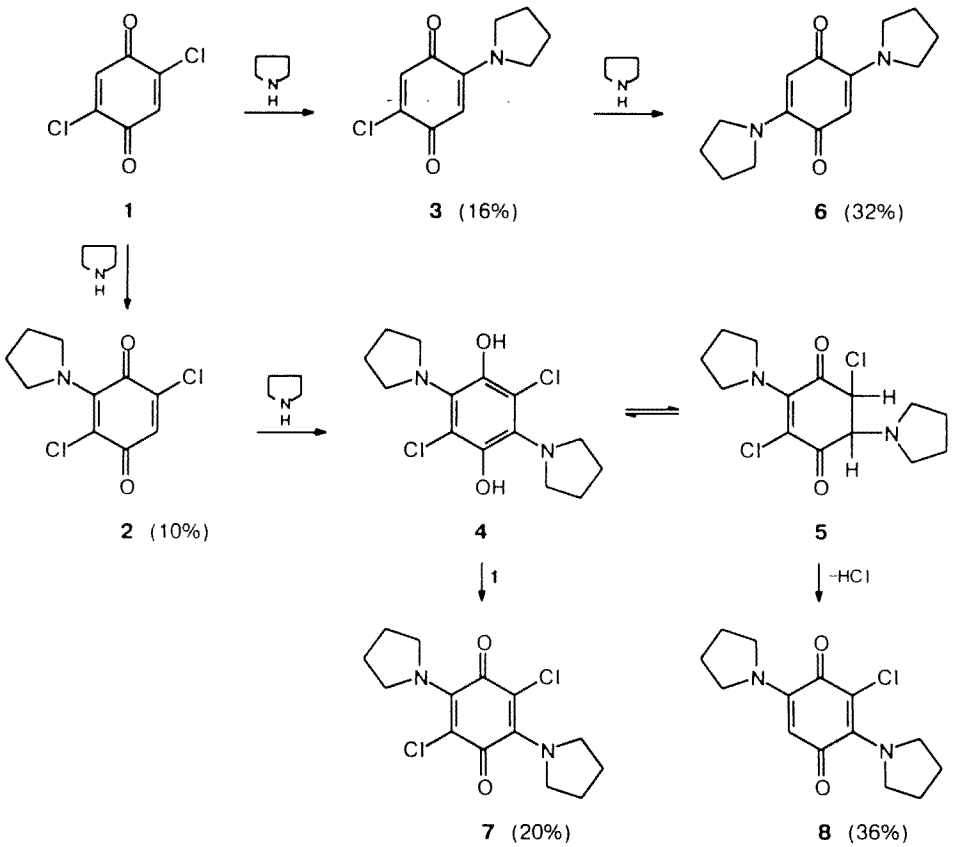
**Scheme 1**

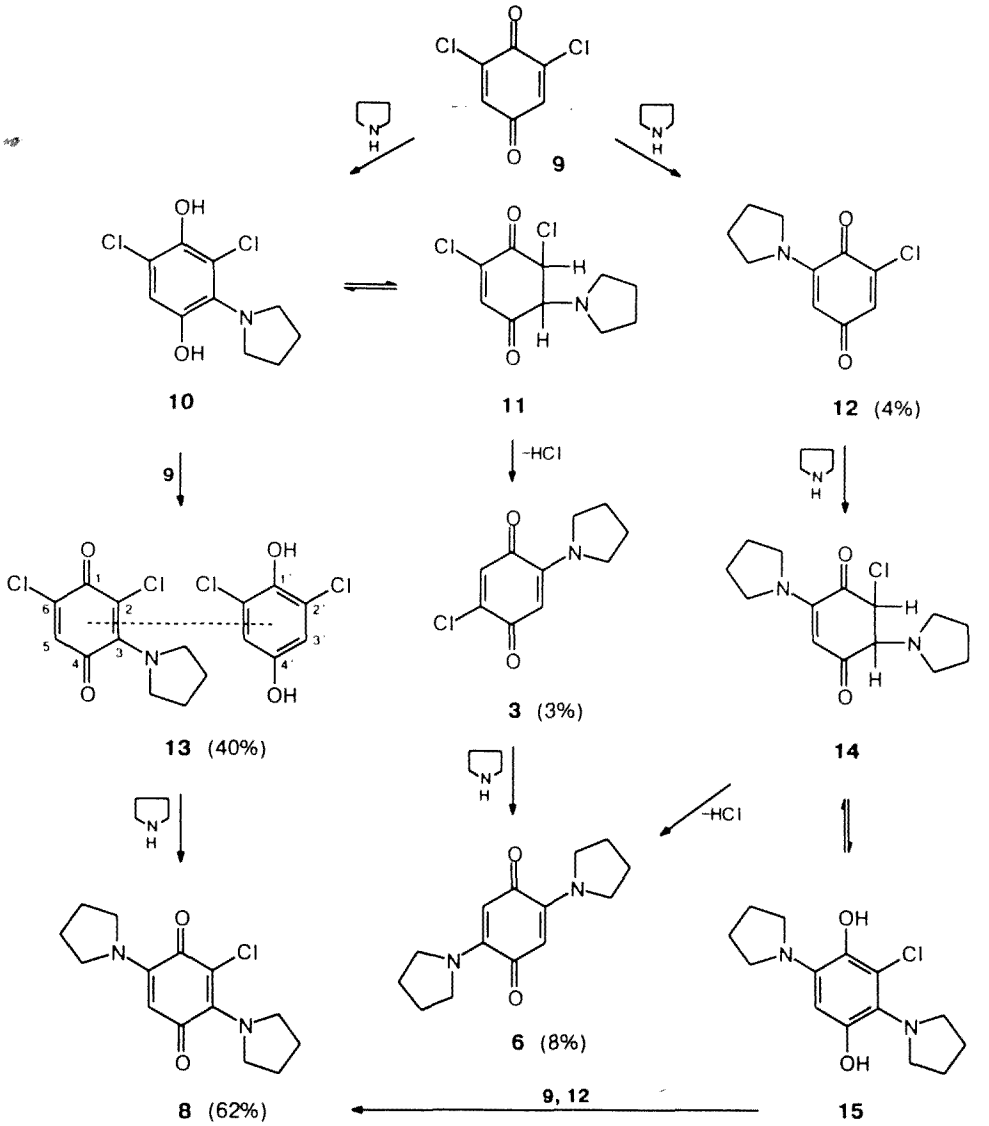



3.95 and 3.27 ppm. This type of effect has been observed previously[7,8] for the $^1$H NMR spectrum of compound **6** and was explained by the fact that the bond between the N atom and the quinone ring is partially double and a dynamic equilibrium exists between the two possible rotamers. By contrast, the protons of the $NCH_2$ group at the *ortho*-position to the chlorine atom in the pyrrolidine fragment give one multiplet at 3.95 ppm similarly to the protons of the $NCH_2$ group of quinone **7**. Taking into account that the presence of the bulky and electron-accepting chlorine atom in the *ortho*-position of the pyrrolidine fragment restricts considerably, as a rule, rotation of this fragment around the bond linking it with the aromatic system,[9,10] it can be assumed that only one rotameric form with a pronounced character of the double bond between the pyrrolidine N atom and the quinone ring is possible for the same pyrrolidine fragments of quinones **7** and **8**. This assumption is confirmed by the values of the chemical shifts for the protons (3.95 ppm) and the carbon atoms (54.5 ppm) of the $NCH_2$ groups in the $^1$H and $^{13}$C NMR spectra of quinones **7** and **8**, which points out a high degree of quaternization of pyrrolidine N atoms in the *ortho*-position to the chlorine atom. It is of interest that the existence of the dynamic equilibrium between rotamers is expressed in the $^{13}$C NMR spectrum of quinone **6** in the fact that the carbon atoms of the $NCH_2$ groups appear as two broadened weak signals at 51.3 and 50.5 ppm. Similarly, the α-C atoms of the pyrrolidine fragment at position 5 of quinone **8** give two broadened signals at 51.6 and 50.6 ppm. By contrast, the α-C atoms of the second pyrrolidine fragment of quinone **8** appear as one intense signal at 54.5 ppm, which is identical to the signal of the α-C carbon atoms of the $NCH_2$ groups of compound **7**.

To elucidate the mechanism of the unexpected formation of compound **8**, we studied the intermediate products in the reaction of dichloroquinone **1** with pyrrolidine. The addition of an insufficient amount (0.5 equiv.) of pyrrolidine to a solution of compound **1** in THF at room temperature resulted in the formation of two new compounds that were violet and crimson-red. In addition, the initial dichloroquinone **1** (70%) and a trace amount (<2%) of the final bisaminoquinone **8** were isolated from the reaction mixture. The spectral data and elemental analysis show that the violet compound is monoaminoquinone **2** (10%) and the red compound corresponds to monoaminoquinone **3** (16%). The reaction of compound **3** with pyrrolidine gave bisaminoquinone **6** in 98% yield, while monoaminoquinone **2** reacts with pyrrolidine to form bisaminoquinone **8** (yield 90%).

The data obtained show that the unexpected formation of aminoquinone **8** in the reaction of compound **1**

**Scheme 2**




with pyrrolidine occurs at the stage of amination of intermediate monoaminoquinone **2** by pyrrolidine. The most probable mechanism for this reaction likely includes the vicinal substitution (*cine*-substitution, $AE_a$-mechanism)[6] of pyrrolidine for the chlorine atom at position 5 of intermediate compound **2** (see Scheme 1).

The products of *cine*-substitution were not observed previously in the reactions of quinone **1** with amines mainly because of the insufficiently high (compared to pyrrolidine) basicity of the amines used previously. Thus, the reaction of compound **1** with morpholine ($pK_a$ = 8.70),[12] which is considerably less basic than pyrrolidine ($pK_a$ = 11.22),[11] resulted in the formation only of 2,5-bis(morpholino)-3,6-dichloro-1,4-benzoquinone and 2,5-bis(morpholino)-1,4-benzoquinone as the final products.[3,5]

In addition to the high basicity of pyrrolidine, one more factor that favors the amination of compound **2** *via* the mechanism of *cine*-substitution is evidently the strong electron-donating effect of the pyrrolidine fragment in a molecule of quinone **2**. As a result of this effect, this quinone becomes unable to oxidize the intermediate hydroquinone **4** to the corresponding bisaminoquinone **7**, which is indicated by the absence of compound **7** among the final products of amination of compound **2** by pyrrolidine. By contrast, the reaction of dichloroquinone **1** with excess pyrrolidine gives bisaminoquinone **7** in 20% yield due to the constant presence of the initial compound **1** in the reaction mixture. The absence of the absorption band corresponding to the n→π*-transition ($S_0 \rightarrow S_1$-type) in the UV spectrum of this compound also indicates that monoaminoquinone **2** cannot oxidize hydroquinone **4**. It is established[13] that it is precisely the band of this transition that characterizes the capability of quinones to serve as oxidants in different redox processes. In the case of strongly conjugated amino-

**Table 1.** UV spectra of monoaminoquinones **2** and **12**

| Compound | $\lambda_{max}$/nm ($\varepsilon$/dm$^3$ mol$^{-1}$ cm$^{-1}$) | | |
|---|---|---|---|
| | $\pi\rightarrow\pi^*$ ($S_0\rightarrow S_1$) | $n\rightarrow\pi^*$ ($S_0\rightarrow S_1$) | $n\rightarrow\pi^*$ ($S_0\rightarrow T_1$) |
| **2** | 298 (7700) | — | 555 (3000) |
| **12** | 292 (7500) | 361 (2200) | 528 (2030) |

quinones, a band of the $n\rightarrow\pi^*$-transition is observed, as a rule, in the range of 350—400 nm.[14] For example, for aminoquinones **6**, **7**, and **8** the bands of the $n\rightarrow\pi^*$-transitions are at 373, 393, and 373 nm, respectively. Meanwhile, the UV spectrum of quinone **2** contains only bands of the $\pi\rightarrow\pi^*$ ($S_0\rightarrow S_1$) and $n\rightarrow\pi^*$ ($S_0\rightarrow T_1$) transitions at 298 and 555 nm, respectively (Table 1).

Based on these spectral parameters, the chemical reactions of compound **2** should most preferably occur to the double bond of its quinone ring.[13] In the reaction of compound **2** with pyrrolidine, this process is the *cine*-substitution of an amino group for the chlorine atom at the double —ClC=CH— bond of quinone **2**. It is noteworthy that there is no published data concerning intermediate products of amination of semi-chlorinated benzoquinones. Since the main products of the amination of dichloroquinone **1** were the corresponding 2,5-bis(amino)-3,6-dichloro-1,4-benzoquinones,[3—5] it was assumed that the primary attack of amines on a molecule of quinone **1** occurs predominantly at positions 3 and 6 of the quinone ring. A comparison of the yields of monoaminoquinones **2** (10%) and **3** (16%) shows clearly that the most reactive positions with respect to amines in a molecule of quinone **1** are in fact positions 2 and 5, the reaction which gives 2-amino-5-chloro-1,4-benzoquinones as the main intermediate product. At the same time, the yield of aminoquinone **6** (32%) in the reaction of dichloroquinone **1** with pyrrolidine is noticeably lower than the total yield of aminoquinones **7** and **8** (56%) formed in the amination of intermediate **2** (see Scheme 1). This is most probably caused by the fact that the reactivity of compound **2** with respect to amines is substantially higher than that of its less chlorinated derivative **3**. This assumption is also favored by the published data,[1,2] according to which an increase in the number of chlorine atoms in the quinone ring is accompanied, as a rule, by an increase in the reactivity of quinones in reactions with nucleophiles.

The reaction of dichloroquinone **9** with excess pyrrolidine was carried out under conditions similar to those of the reaction with quinone **1**. Bisaminoquinone **6** was obtained in 8% yield along with the expected bisaminoquinone **8** (yield 62%). Unlike quinone **1**, compound **9** reacted with an insufficient amount of pyrrolidine to form three products: one violet and two crimson-red compounds. In addition, the initial dichloroquinone **9** (48%) and a trace amount of quinone **8** (<2%) were isolated from the reaction mixture. The spectral data and elemental analysis showed that the red compounds are monoaminoquinones **3** and **12**, while the violet compound is a quinhydrone complex of 2,6-dichloro-3-pyrrolidino-1,4-benzoquinone with 2,6-dichlorohydroquinone (**13**).

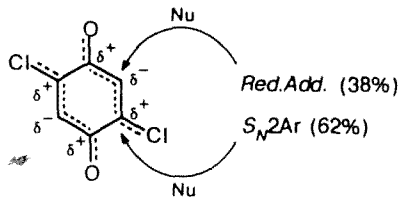
All signals in the $^1$H and $^{13}$C spectra of complex **13** were assigned using the nuclear Overhauser effect and two-dimensional CH-COSY spectroscopy. The isolation of complex **13** from the reaction of quinone **9** with pyrrolidine is the first example of obtaining stable quinhydrone complexes in reactions of quinones with amines. Previously, the participation of the initial quinones as external oxidants in the reductive addition of amines to quinones was proved only by the data on the formation of free hydroquinones in these reactions.[1,2] The analysis of UV, IR, and $^1$H and $^{13}$C NMR spectra of complex **13** makes it possible to assume that, similarly to many other quinhydrone complexes,[15] quinone and hydroquinone molecules are bound in complex **13** predominantly *via* hydrogen bonds and intermolecular Cl—Cl contacts without a noticeable transfer of charge between the components of the complex.

The formation of compounds **3**, **12**, and **13** as intermediate products of the amination of quinone **9** by pyrrolidine testifies that the reaction involves three different competing processes even at the stage of the insertion of the first amino group into a molecule of quinone **9**. The main direction of the reaction is the reductive addition of a pyrrolidine molecule to position 3 of quinone **9**. The product of this reaction, hydroquinone **10**, reacts with the initial dichloroquinone **9** to give complex **13** in 40% yield.

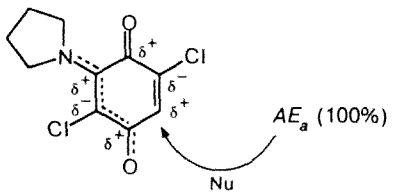
The second direction of the reaction includes the nucleophilic replacement of the chlorine atom at position 2 of quinone **9** by a pyrrolidine fragment *via* direct attack of pyrrolidine on this position ($S_N$2Ar mechanism). The low yield of monoaminoquinone **12** formed (4%) indicates that positions 2 and 6 in a molecule of dichloroquinone **9** have the lowest reactivity with respect to amines.

The basic difference between the reactions of diichloroquinones **1** and **9** with pyrrolidine is the formation of the product of *cine*-substitution, monoaminoquinone **3** (yield 3%), at the stage of the primary attack on a molecule of quinone **9** by pyrrolidine. This result shows that the capability of chloroquinones to give products of *cine*-substitution in reactions with amines is determined by the properties of the chloroquinones rather than the basicity of the amines used. It has been established[16] that, unlike dichloroquinone **9**, in a molecule of quinone **1** the conjugation between the chlorine atoms and carbonyl groups manifests itself more noticeably due to which the structure of compound **1** resembles strongly conjugated 2,5-bis(amino)-1,4-benzoquinones (Scheme 3). It is known[13] that in this type of system positive charges in the quinone ring are located on the C(1), C(2), C(4), and C(5) atoms, while negative charges are located on the C(3) and C(6) atoms. These data explain why monoaminoquinone **3** is the main

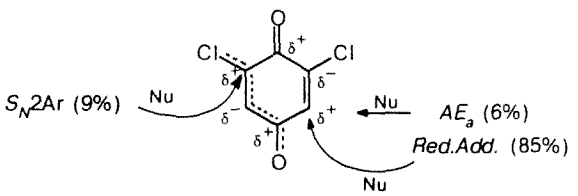
**Scheme 3***




**1**




**2**




**9**

intermediate product of the reaction of quinone **1** with pyrrolidine.

By contrast, only one of the chlorine atoms is predominantly involved in conjugation with the carbonyl group in quinone **9**, and the degree of this conjugation is considerably weaker than in dichloroquinone **1** (see Scheme 3).[16] Compared to quinone **1**, the double bonds of the quinone ring of compound **9** are more localized and considerably less activated for direct nucleophilic substitution *via* the $S_N2Ar$ mechanism. As a rule, the $AE_a$ mechanism is rather typical of this type of unactivated double bonds.[6] It can be assumed that it is precisely this higher degree of localization of the π-bonds in a molecule of quinone **9** which causes this compound to be able to form products of *cine*-substitution in low yields in reactions with strong amines.

The validity of this assumption is favored by the reaction of monoaminoquinone **2** with pyrrolidine. According to the data of structural studies,[17] molecules of monoaminoquinones contain a strongly conjugated structural trimethinomerocyanine fragment and a highly localized double bond. As the reaction of monoaminoquinone **2** with pyrrolidine shows, it is precisely the attack of amine on this localized double bond of quinone **2** that causes the formation of the product of *cine*-substitution in 90% yield (see Scheme 3).

* Directions of the nucleophilic attack on molecules of quinones **1**, **2**, and **9** by pyrrolidine.

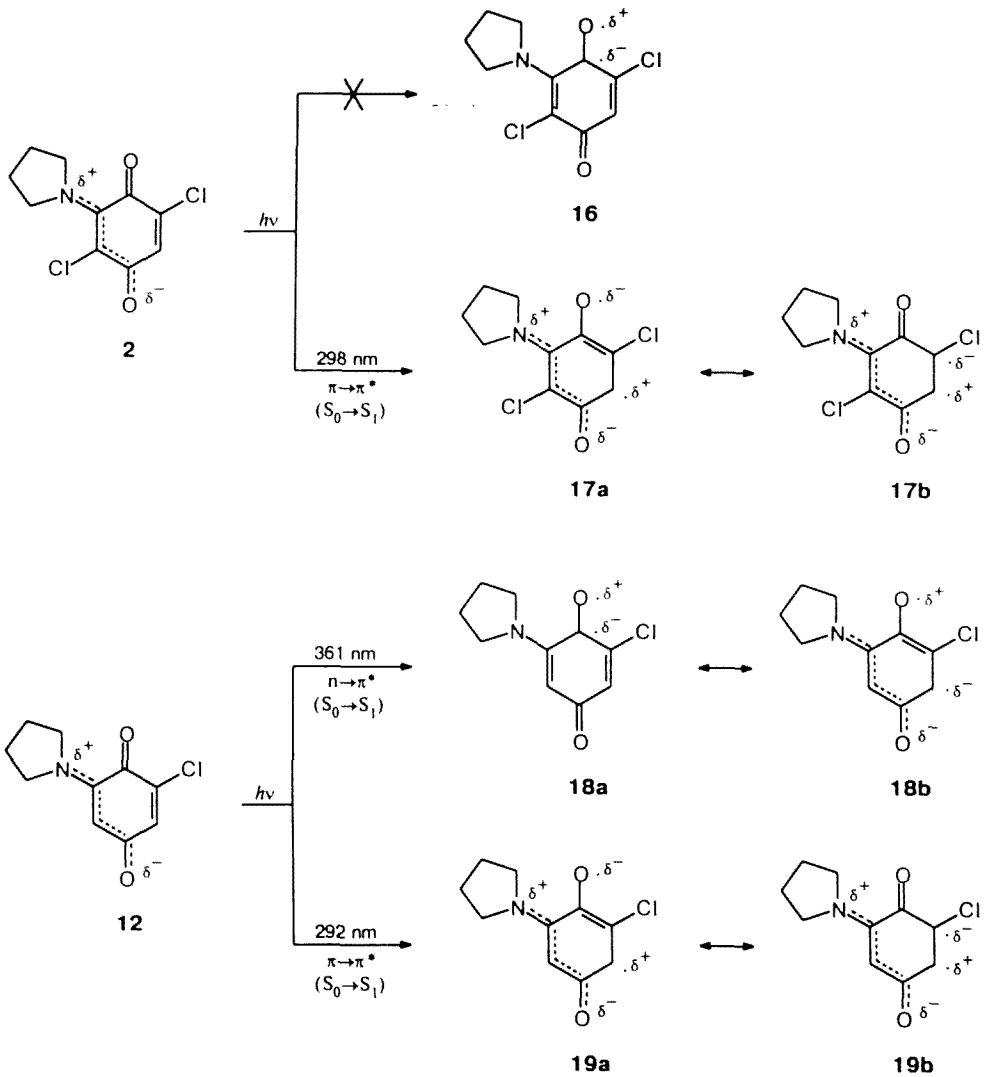
The analysis of the intermediate products of amination of quinone **9** by pyrrolidine indicates that one of the reasons for the unexpected formation of bisaminoquinone **6** in the reaction of compound **9** with excess pyrrolidine is the *cine*-substitution of pyrrolidine in the initial quinone **9** followed by the nucleophilic substitution of the given amine in monoaminoquinone **3** *via* the $S_N2Ar$ mechanism. As might be expected, the reaction of complex **13** with pyrrolidine gave only bisaminoquinone **8** in 98% yield (see Scheme 2). The existence of the hydroquinone component in complex **13** virtually did not hinder the nucleophilic replacement of the chlorine atom by an amino group in a molecule of 2,6-dichloro-3-pyrrolidino-1,4-benzoquinone.

The most interesting result was obtained for the reaction of monoaminoquinone **12** with pyrrolidine. Unlike monoaminoquinone **2**, compound **12** reacted with pyrrolidine to give bisaminoquinones **6** and **8** in 15 and 30% yields, respectively (see Scheme 2). The principal peculiarity of this reaction is the fact that it involves two competing processes. The reductive addition of a pyrrolidine molecule to position 3 of quinone **12** gives bisaminoquinone **8** as the main product. A less preferable process is the *cine*-substitution of pyrrolidine for the chlorine atom at position 2 of quinone **12** resulting in the formation of bisaminoquinone **6**.

These data show that the capability of monoaminoquinones to form products of *cine*-substitution in amination reactions decreases substantially when these compounds gain oxidation properties. The band of the n→π*-transition ($S_0 \rightarrow S_1$) at 361 nm in the UV spectrum of monoaminoquinone **12** indicates the existence of these properties (Table 1). The most probable reason for such a considerable difference in the UV spectral parameters of monoaminoquinones **2** and **12** and in their reactivity with respect to amines is the different strengths of conjugation of the amino substituent with the carbonyl group in the molecules of these compounds. We have previously shown[10] that the presence of strong electron-accepting substituents, for example, a chlorine atom or cyano group, at the *ortho*-position to the pyrrolidine fragment of quinones enhances considerably the degree of this conjugation in aminoquinone molecules. According to these data, the absence of a band of the n→π*-transition in the UV spectrum of the more conjugated quinone **2** is likely caused by the considerable energy expenditure necessary to overcome the strong conjugation in molecules of this compound to photogenerate n→π*-type biradicals **16** (Scheme 4). Therefore, the process that gives the π→π*-type biradicals **17a** and **17b** turns out to be energetically more favorable for molecules of quinone **2**.

It has been established[13] that quinones for which the π-π*-type ($S_0 \rightarrow S_1$) transition is energetically more favorable are involved in many chemical reactions involving exclusively the double bonds of the quinone ring. Since the primary act in the reactions of quinones with amines is the transfer of an electron from the amine

**Scheme 4**




molecule to the quinone molecule,[18–20] these reactions obey in many respects the same laws that are fulfilled for photochemical transformations of quinones.[13] In the case of aminoquinone **2**, this manifests itself in the fact that in the reaction with pyrrolidine the reaction centers of quinone **2** are positions 5 and 6 of the quinone ring and the only reaction products are the products of *cine*-substitution. By contrast, a molecule of a less conjugated aminoquinone, **12**, exhibits the capability of forming both biradicals **19a** and **19b** and biradicals **18a** and **18b** (see Scheme 4). In the chemical transformations of the latter, the carbonyl group and the C(3) atom of the quinone fragment serve, as a rule, as reaction centers.[13] A typical reaction involving the carbonyl group of quinones is the oxidation of hydroquinones by quinones.[13] In the case of the reaction of aminoquinone **12** with pyrrolidine (see Scheme 2), hydroquinone **15** is oxidized by the initial aminoquinone to form the final product **8**. The low yield of compound **8** (30%) attests to the low oxidation capability of monoaminoquinone **2**. The competing process is the *cine*-substitution of pyrrolidine in quinone **12**. The higher (compared to dichloroquinone **9**) degree of localization of the double bond in molecules of aminoquinone **12** [16,17] causes a higher yield of the product of *cine*-substitution in the amination of the latter. It is noteworthy that even the exceptionally high oxidation capability of dichloroquinone **9** [1,2] does not completely suppress the process of *cine*-substitution, but only decreases considerably the yield of the product of this reaction.

Despite the fact that all conclusions that monoaminoquinone **2** cannot serve as an oxidant at the stage of oxidation of bisaminated hydroquinone to the corresponding bisaminoquinone were based only on the data of analysis of the products of amination and the UV spectrum of quinone **2**, a polarographic study[21] of a series of monoaminoquinones and their 2,5-bisaminated derivatives showed that the reduction potential of some

monoaminoquinones in fact can be more negative than the potential of the respective bisaminoquinones. The possibility of the existence of these anomalous properties of monoaminoquinones is indicated, in particular, by the capability of some monoaminoquinones to spontaneously disproportionate to the corresponding 2,5-bisaminoquinones.[22] It is likely that the most probable mechanism of this rearrangement includes [2+2]-biscycloaddition of two aminoquinone molecules followed by the cyclodecomposition of a molecule of the dimer to form 2,5-bisaminoquinone and benzoquinone molecules.[13,23] On the whole, the disproportionation reactions of several monoaminoquinones attest exclusively to the $\pi\rightarrow\pi^*$-type reactivity of these compounds.[13] In this context, the amination of monoaminoquinone **2** by pyrrolidine *via* the *cine*-substitution mechanism is another example of the characteristic reactions of quinones that possess pronounced $\pi\rightarrow\pi^*$-type reactivity.

The results obtained in this work show that along with the previously known mechanisms of reductive addition of amines to quinones and nucleophilic substitution of amino groups for chlorine atoms *via* the $S_N2Ar$ mechanism, one more possible direction of reactions of chloroquinones with amines can be *cine*-substitution of amino groups for chlorine atoms in molecules of the initial chloroquinones and in the products of their intermediate amination. The main factor determining the direction of reactions of chloroquinones with amines *via* the mechanism of *cine*-substitution is the high basicity of the amines used. In reactions with such amines, the capability of chloroquinones to form products of *cine*-substitution is determined both by the degree of localization of the π-bonds in the molecules of the initial compounds and the redox properties of the intermediate monoaminoquinones. Enhancement of the conjugation effect in monoaminoquinone molecules weakens the oxidation capability of these compounds and shifts the direction of amination reactions to the formation of products of *cine*-substitution.

## Experimental

$^1H$ and $^{13}C$ NMR spectra were recorded on a Jeol EX-270 instrument with working frequencies of 270 MHz ($^1H$, $SiMe_4$ as the internal standard) and 67.8 MHz ($^{13}C$). IR spectra were recorded on a Perkin-Elmer 983 instrument in KBr. Electronic absorption spectra were recorded on a Hitachi U-3400 instrument in $CH_2Cl_2$. Mass spectra were recored on a Jeol JMS-DX 303 instrument; the energy of ionizing electrons was 70 eV.

**Reaction of 2,5-dichloro-1,4-benzoquinone 1 with excess pyrrolidine.** Pyrrolidine (0.284 g, 4.0 mmol) was added with stirring to a solution of compound **1** (0.177 g, 1.0 mmol) in THF (50 mL) in an atmosphere of nitrogen. The reaction mixture obtained was kept in the dark for 6 h at ~20 °C, then the solvent was distilled off at a reduced pressure, and the residue was chromatographed on a column with silica gel using a hexane—ethyl acetate (1 : 1) system as the eluent. Three products were obtained.

**2,5-Bis(pyrrolidino)-1,4-benzoquinone (6).** The yield was 79 mg (32%); $R_f$ 0.31; m.p. 267—268 °C (from THF). IR (KBr), $\nu/cm^{-1}$: 2975, 2954, 2879, 2847 (C—H), 1614 (C=O), 1558 (C=C). EAS ($CH_2Cl_2$), $\lambda_{max}/nm$ (ε): 507 (490), 373 (26600), 226 (27900). $^1H$ NMR ($CDCl_3$), δ: 5.30 (s, 2 H, H-3 and H-6); 4.00 (br.s, 4 H, $NCH_2$); 3.31 (br.s, 4 H, $NCH_2$); 1.94 (m, 8 H, $CH_2$). $^{13}C$ NMR ($CDCl_3$), δ: 180.4 (C-1); 149.7 (C-2); 99.7 (C-3); 51.3 and 50.5 ($NCH_2$); 26.6 and 23.7 ($CH_2$). MS (*m/z*, $I_{rel}$(%)): 246 (75) $M^+$. Found (%): C, 68.20; H, 7.33; N, 11.31. $C_{14}H_{18}N_2O_2$. Calculated (%): C, 68.29; H, 7.32; N, 11.38.

**2,5-Bis(pyrrolidino)-3,6-dichloro-1,4-benzoquinone (7).** The yield was 21 mg (20%); $R_f$ 0.71; m.p. 178—180 °C (from a benzene—hexane mixture). IR (KBr), $\nu/cm^{-1}$: 2967, 2949, 2875 (C—H), 1631 (C=O), 1533 (C=C). EAS ($CH_2Cl_2$), $\lambda_{max}/nm$ (ε): 546 (958), 393 (19200), 303 (12800), 228 (13800). $^1H$ NMR ($CDCl_3$), δ: 3.96 (m, 8 H, $NCH_2$); 1.90 (m, 8 H, $CH_2$). $^{13}C$ NMR ($CDCl_3$), δ: 175.1 (C-1); 149.9 (C-2); 101.5 (C-3); 54.4 ($NCH_2$); 25.5 ($CH_2$). MS (*m/z*, $I_{rel}$(%)): 314 (47) $M^+$. Found (%): C, 53.24; H, 5.08; N, 8.83. $C_{14}H_{16}Cl_2N_2O_2$. Calculated (%): C, 53.33; H, 5.08; N, 8.85.

**2,5-Bis(pyrrolidino)-3-chloro-1,4-benzoquinone (8).** The yield was 51 mg (36%); $R_f$ 0.50; m.p. >350 °C (from a benzene—hexane mixture). IR (KBr), $\nu/cm^{-1}$: 2971, 2871 (C—H), 1627 (C=O), 1579, 1526 (C=C). EAS ($CH_2Cl_2$), $\lambda_{max}/nm$ (ε): 532 (1700), 373 (15000), 254 sh (10300), 233 (13900). $^1H$ NMR ($CDCl_3$), δ: 5.22 (s, 1 H, H-6); 3.95 (m, 6 H, $NCH_2$); 3.27 (br.s, 2 H, $NCH_2$); 1.93 (m, 4 H, $CH_2$); 1.86 (s, 4 H, $CH_2$). $^{13}C$ NMR ($CDCl_3$), δ: 180.2 (C-1); 174.9 (C-4); 149.1 (C-2); 148.9 (C-5); 105.0 (C-3); 97.9 (C-6); 54.5, 51.6 and 50.6 ($NCH_2$); 26.6, 25.6 and 23.7 ($CH_2$). MS (*m/z*, $I_{rel}$(%)): 282 (32) $(M+2)^+$; 280 (80) $M^+$. Found (%): C, 59.62; H, 6.10; N, 9.76. $C_{14}H_{17}ClN_2O_2$. Calculated (%): C, 59.89; H, 6.06; N, 9.98.

**Reaction of dichloroquinone 1 with an insufficient amount of pyrrolidine.** The reaction of compound **1** (1.77 g, 10.0 mmol) with pyrrolidine (0.35 g, 5 mmol) was carried out under conditions similar to those described above. Two new compounds (**2** and **3**) were obtained along with the initial compound **1** (1.24 g, 70%) and traces of compound **8** (20 mg, <2%).

**2,5-Dichloro-3-pyrrolidino-1,4-benzoquinone (2).** The yield was 120 mg (10%); $R_f$ 0.78; m.p. 86.5—87.5 °C (from pentane). IR (KBr), $\nu/cm^{-1}$: 3046, 2957, 2927, 2878 (C—H), 1690 and 1630 (C=O), 1600 and 1523 (C=C). $^1H$ NMR ($CDCl_3$), δ: 7.03 (s, 1 H, H-6); 3.92 (s, 4 H, $NCH_2$); 1.93 (m, 4 H, $CH_2$). $^{13}C$ NMR ($CDCl_3$), δ: 177.5 (C-4); 176.6 (C-1); 146.4 (C-3); 138.7 (C-5); 134.1 (C-6); 109.2 (C-2); 54.3 ($NCH_2$); 25.7 ($CH_2$). MS (*m/z*, $I_{rel}$(%)): 245 (45) $M^+$. Found (%): C, 48.75; H, 3.75; N, 5.55. $C_{10}H_9Cl_2NO_2$. Calculated (%): C, 48.81; H, 3.69; N, 5.69.

**2-Chloro-5-pyrrolidino-1,4-benzoquinone (3).** The yield was 340 mg (16%); $R_f$ 0.58; m.p. 141—142 °C (from pentane). IR (KBr), $\nu/cm^{-1}$: 3067, 3031, 2981, and 2870 (C—H), 1661 and 1616 (C=O), 1599 and 1565 (C=C). EAS ($CH_2Cl_2$), $\lambda_{max}/nm$ (ε): 523 (2600), 288 (6050), 232 (15300). $^1H$ NMR ($CDCl_3$), δ: 6.75 (s, 1 H, H-3); 5.60 (s, 1 H, H-6); 3.86 and 3.31 (d. br.s, 4 H, $NCH_2$); 1.99 (m, 4 H, $CH_2$). $^{13}C$ NMR ($CDCl_3$), δ: 182.7 (C-4); 176.1 (C-1); 147.5 (C-5); 147.4 (C-2); 130.1 (C-3); 101.0 (C-6); 51.1 ($NCH_2$); 26.6 и 23.7 ($CH_2$). MS (*m/z*, $I_{rel}$(%)): 211 (65) $M^+$. Found (%): C, 56.72; H, 4.79; N, 6.47. $C_{10}H_{10}ClNO_2$. Calculated (%): C, 56.77; H, 4.73; N, 6.62.

**Reaction of compound 2 with pyrrolidine.** The reaction of compound **2** (61 mg, 0.25 mmol) with pyrrolidine (70 mg, 1 mmol) was performed under conditions similar to those described above. Compound **8** (63 mg, 90%) was obtained.

**Reaction of compound 3 with pyrrolidine.** The reaction of compound **3** (0.211 g, 1.0 mmol) with pyrrolidine (0.284 g, 4 mmol) was performed under the conditions similar to those described above. Compound **6** (240 g, 98%) was obtained.

**Reaction of dichloroquinone 9 with excess pyrrolidine.** The reaction of compound **9** (0.177 g, 1.0 mmol) with pyrrolidine (0.284 g, 4 mmol) was performed under conditions similar to those described above. Compounds **6** (20 mg, 8%) and **8** (87 mg, 62%) were obtained.

**Reaction of dichloroquinone 9 with an insufficient amount of pyrrolidine.** The reaction of compound **9** (1.77 g, 10.0 mmol) with pyrrolidine (0.35 g, 5 mmol) was performed under conditions described above. Two new compounds (**12** and **13**) were obtained along with the initial compound **9** (850 mg, 48%) and compounds **3** (60 mg, 3%) and **8** (20 mg, <2%) described previously.

**2-Chloro-6-pyrrolidino-1,4-benzoquinone (12).** The yield was 84 mg (4%); $R_f$ 0.45; m.p. 132—133 °C (from pentane). IR (KBr), $\nu/cm^{-1}$: 2961, 2925 and 2858 (C—H), 1690 and 1620 (C=O), 1600 and 1549 (C=C). $^1H$ NMR ($CDCl_3$), δ: 6.87 (d, 1 H, H-3, $^3J_{H,H}$ = 2.3 Hz); 5.49 (d, 1 H, H-5, $^3J_{H,H}$ = 2.3 Hz); 3.96 and 3.30 (d. br.s, 4 H, $NCH_2$); 1.98 (m, 4 H, $CH_2$). MS (*m/z*, $I_{rel}$(%)): 211 (55) $M^+$. Found (%): C, 56.70; H, 4.80; N, 6.54. $C_{10}H_{10}ClNO_2$. Calculated (%): C, 56.77; H, 4.73; N, 6.62.

**Quinhydrone complex 13.** Yield 170 mg (40%); $R_f$ 0.76; m.p. 103—104 °C (from pentane). IR (KBr), $\nu/cm^{-1}$: 3400 (O—H), 2985 и 2870 (C—H), 1675 (C=O), 1588 и 1516 (C=C), 1481, 1448, 1375, 1341, 1321, 1250, 1234, 1220, 1052, 951, 901, 876, 864, 855, 804, 789, 762, 703. EAS ($CH_2Cl_2$), $\lambda_{max}$/nm (ε): 542 (580), 368 (815), 298 (4600). $^1H$ NMR ($CDCl_3$), δ: 6.85 (s, 2 H, H-3′); 6.74 (s, 1 H, H-5); 5.90 (br.s, 1 H, OH); 5.50 (br.s, 1 H, OH); 3.93 (s, 4 H, $NCH_2$); 1.93 (m, 4 H, $CH_2$). $^{13}C$ NMR ($CDCl_3$), δ: 181.9 (s, C-4); 171.7 (d, C-1, $^3J_{C,H}$ = 5.5 Hz); 149.4 (m, C-3); 146.8 (d, C-2′, $^2J_{C,H}$ = 4.9 Hz); 145.8 (d, C-6, $^2J_{C,H}$ = 5.5 Hz); 141.7 (t, C-6′, $^3J_{C,H}$ = 7.3 Hz); 129.6 (d, C-5, $^1J_{C,H}$ = 175.8 Hz); 120.9 (m, C-2′); 115.6 (d.d, C-3′, $^1J_{C,H}$ = 166.6 Hz, $^3J_{C,H}$ = 5.5 Hz); 107.6 (s, C-2); 54.5 (m, $NCH_2$, $^1J_{C,H}$ = 145.9 Hz); 25.5 (m, $CH_2$, $^1J_{C,H}$ = 134.0 Hz). MS (*m/z*, $I_{rel}$(%)): 245 (85) $Q^+$, 178 (90) $HQ^+$. Found (%): C, 45.09; H, 3.21; N, 3.16. $C_{16}H_{13}Cl_4NO_4$. Calculated (%): C, 45.20; H, 3.06; N, 3.30.

**Reaction of compound 12 with pyrrolidine.** The reaction of compound **12** (53 mg, 0.25 mmol) with pyrrolidine (70 mg, 1 mmol) was performed under conditions similar to those described above. Compounds **6** (10 mg, 15%) and **8** (11 mg, 30%) were obtained.

**Reaction of compound 13 with pyrrolidine.** The reaction of compound **13** (106 mg, 0.25 mmol) with pyrrolidine (70 mg, 1 mmol) was performed under conditions similar to those described above. Compound **8** (69 mg, 99%) was obtained.

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