Intermediates in the Reactions of Chloranil and 2,6-Dichloro-1,4-benzoquinone with Pyrrolidine

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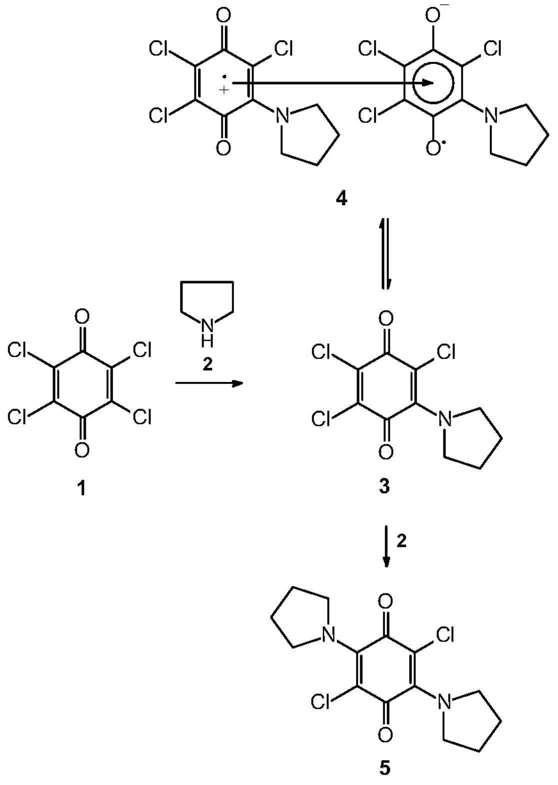
Although the intermediates in the reactions of chloranil and 2,6-dichloro-1,4-benzoquinone with pyrrolidine are the corresponding monoaminated chloroquinones, these compounds exhibit a pronounced tendency to form molecular complexes; thus, the spectral characteristics of 2,3,5-trichloro-6-pyrrolidino-1,4-benzoquinone indicate its partial self-complexation into the corresponding biradical dimer. 2,6-Dichloro-3-pyrrolidino-1,4-benzoquinone forms a stable quinhydrone complex with 2,6-dichlorohydroquinone.

The nucleophilic substitution of chloro-1,4-benzoquinones (CBQ) by aliphatic and aromatic amines is of considerable interest and has been extensively studied.[1] The first step of the reaction has been shown to involve electron-transfer from amine to quinone.[2] Investigations of the further reaction pathway were limited only to spectroscopic studies[3,4] and all attemps to isolate any intermediates from the reactions were unsuccessful. As a result, two different hypotheses have been proposed for possible intermediates in these reactions, the first involving monoaminated CBQ[2] and the other, charge-transfer (CT) complexes.[3,4] The aim of the present work was therefore to develop a method of isolation of the intermediates in the reactions of CBQ with aliphatic amines and to study the structure and properties of these intermediates. The reactions of chloranil **1** and 2,6-dichloro-1,4-benzoquinone **6** with pyrrolidine have been chosen as two model reactions.



Scheme 1

The study of the reaction of **1** with **2** showed that when a deficit of amine (molar ration of amine:quinone, 1:2) was added to a solution of **1** in THF, a single, new compound of violet colour was formed. Separation of the components of the reaction mixture by column chromatography allowed the isolation of this compound along with starting **1** (97%) and trace amounts of the final **5** (<1%). The elemental analysis and spectroscopic data[†] show the violet compound to be quinone **3** (3% yield). The reaction of **3** with **2** gave the final quinone **5** in quantitative yield.

The formation of violet CT-complexes in the reaction of **1** with aromatic amines is well-known from the literature.[5] It has also been shown that some aminoquinones can play not only the traditional role of electron-acceptor but the typical (for aromatic amines) role of electron-donor as well.[6] As can be seen from the spectral data of **3**,[†] this compound exhibits a tendency to form CT-complexes due to its partial self-complexation into dimer **4**. Thus, the UV-VIS spectrum of **3** shows the presence of a broad absorption band extending from 440 to 700 nm with its peak at 566.4 nm ($\varepsilon = 3080$), very characteristic of CT-complexes of **1** with aromatic amines.[7] The EPR spectrum of **3** displays a relatively strong signal at $g = 2.0068$ which has a close resemblence to EPR signals of some conjugated polyaminoquinones which form biradicals due to charge-transfer between two neighbouring quinone macromolecules.[8] These data demonstrate that the hypothesis proposed earlier for the intermediate CT-complex formation in the reactions of **1** with aliphatic amines[3,4] can be also considered to be true.

In the reactions of **6** with **2** could be expected *a priori* two different directions of initial attack of **6** by **2**: (i) nucleophilic substitution of the chlorine atom at position **2** and (ii) the reductive addition of amine at position 3.[1] Another interesting question which needed to be explained was the unexpected formation of quinone **12** (8%) along with quinone **11** (62%) as the final products in the reaction of **6** with excess of **2**. The reaction of **6** with a deficit of **2** (2:1) showed that two new compounds of violet and purple colour are formed in the reaction along with the presence in the reaction mixture of starting **6** (48%) and a trace amount of final **11** (2%). The elemental analysis and spectroscopic data[‡] showed the violet compound to be the complex of 2,6-dichloro-3-pyrrolidino-1,4-benzoquinone with 2,6-dichlorohydroquinone **9**, whereas the purple colour was the quinone **10**. One can see that the general

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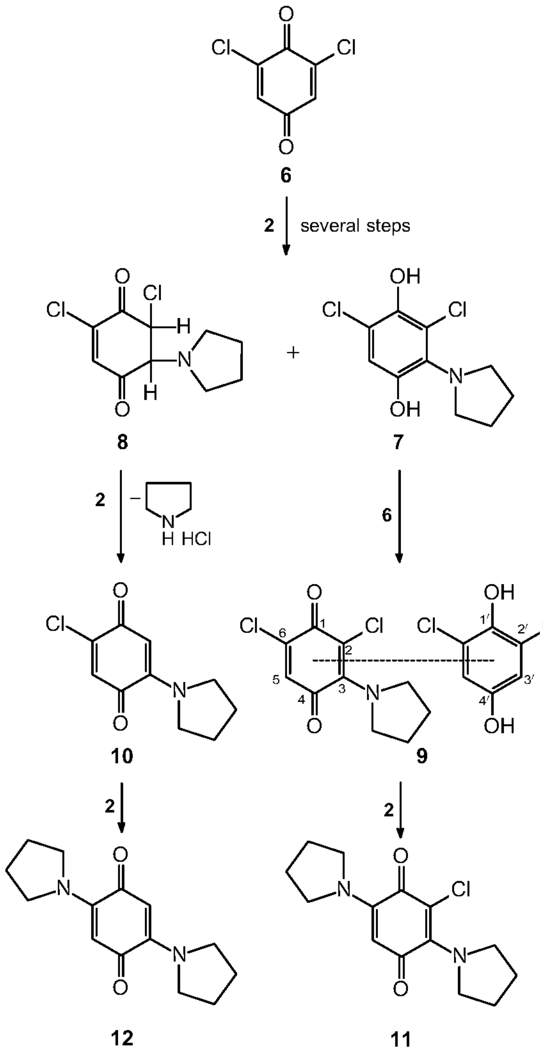
[†] Characteristic data for compound **3**: m.p. 132.5–133.5 °C (decomp.); UV-VIS (CH_2Cl_2) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 566 (3080), 307 (7000), 271 (15900); IR ν_{max}/cm^{-1} 2971, 2859, 1691, 1618, 1604, 1525, 1473, 1454, 1377, 1343, 1326, 1276, 1209, 1070, 930, 862, 804, 748, 732, 724; ^{1}H NMR ($CDCl_3$) δ 3.93 (m, 4H, α-CH_2), 1.95 (m, 4H, β-CH_2); ^{13}C NMR ($CDCl_3$) δ 175.6 (C-1), 170.0 (C-4), 146.4 (C-6), 142.1 (C-3), 135.7 (C-2), 107.7 (C-5), 54.6 (α-CH_2), 25.6 (β-CH_2). Satisfactory elemental analyses were obtained.

[‡] Characteristics for compounds **9–12**. **9**: m.p. 103–104 °C (decomp.); UV-VIS (CH_2Cl_2) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 541.8 (580), 368 (815), 298.2 (4600); IR ν_{max}/cm^{-1} 3400, 2985, 2870, 1675, 1588, 1516, 1481, 1448, 1375, 1341, 1321, 1250, 1234, 1220, 1052, 951, 901, 876, 864, 855, 804, 789, 762, 703; ^{1}H NMR ($CDCl_3$) δ 6.85 (s, 2H, H-3′), 6.74 (s, 1H, H-5), 5.90 (br s, 1H, OH), 5.50 (br s, 1H, OH), 3.93 (m, 4H, α-CH_2), 1.93 (m, 4H, β-CH_2); ^{13}C NMR ($CDCl_3$) δ 181.9s (C-4), 171.7d (C-1, ^3J 5.5 Hz), 149.4m (C-3), 146.8d (C′-4, ^2J 4.9 Hz), 145.8d (C-6, ^2J 5.5 Hz), 141.7t (C′-1, ^3J 7.3 Hz), 129.6d (C-5, ^1J 175.8 Hz), 120.9m (C′-2), 115.6dd (C′-3, ^1J 166.6 Hz, ^3J 5.5 Hz), 107.6s (C-2), 54.5m (α-CH_2, ^1J 145.9 Hz), 25.5m (β-CH_2, ^1J 134 Hz).



Scheme 2

direction in the reaction of **6** with **2** is the attack by **2** of position 3 in **6**. The further reaction pathway has two directions. (i) The oxidation of hydroquinone **7** by starting **6** gives quinhydrone **9** in 40% yield. (ii) The loss of HCl by the intermediate **8** is the less preferable process in terms of a deficit of **2** and gives **10** only in 3% yield. The reactions of **9** and **10** with **2** gave the final **11** and **12** in 95% and 98% yields, respectively. The isolation of quinhydrone **9** is the first example of isolation of quinhydrones in the reactions of quinones with nucleophiles. The precise assignment of all signals in the NMR spectra of **9** was performed by use of NOE and CH-COSY NMR techniques.‡ Similar to the other hydrogen-bonded quinhydrones,[7] quinhydrone **9** does not display paramagnetic properties. Once again, the formation of stable **9** indicates the strong tendency for monoaminated CBC to form molecular complexes noted earlier by analysis of the spectra of **3**.

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10: m.p. 141–142 °C (decomp.); UV-VIS (CH_2Cl_2) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 523 (2600), 288 (6050), 232 (15300); IR ν_{max}/cm^{-1} 3067, 3031, 2981, 2870, 1661, 1616, 1599, 1565, 1452, 1412, 1363, 1321, 1256, 1240, 1208, 1177, 1123, 1102, 1042, 1009, 921, 885, 829, 805, 760, 705, 669; ^{1}H NMR ($CDCl_3$) δ 6.75 (s, 1H, H-3), 5.60 (s, 1H, H-6), 3.86 and 3.31 (d br s, 4H, α-CH_2), 1.99 (m, 4H, β-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 (α-CH_2), 26.6 and 23.7 (β-CH_2).

11: m.p. 267–268 °C (decomp.); UV-VIS (CH_2Cl_2) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 507 (490), 373 (26600), 226 (27900); IR ν_{max}/cm^{-1} 2975, 2954, 2879, (C–H), 1614 (C=O), 1558 (C=C); ^{1}H NMR ($CDCl_3$) δ 5.30 (s, 2H, H-3), 4.00 (br s, 4H, α-CH_2), 3.31 (br s, 4H, α-CH_2), 1.94 (m, 8H, β-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 (α-CH_2), 26.6 and 23.6 (β-CH_2).

12: reddish brown needles (from THF–water), at 168 °C phase transfer into dense red needles being stable without melting up to 400 °C; UV-VIS (CH_2Cl_2) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 532 (1700), 373 (15000), 254sh (10300), 233 (13900); IR ν_{max}/cm^{-1} 2971, 2871 (C–H), 1627, 1579 (C=O), 1526 (C=C); ^{1}H NMR ($CDCl_3$) δ 5.22 (s, 1H, H-6), 3.95 (br s, 6H, α-CH_2), 3.27 (br s, 2H, α-CH_2), 1.93 (m, 4H, β-CH_2), 1.86 (m, 4H, β-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 (α-CH_2 vicinal to Cl), 51.6 and 50.6 (α-CH_2 vicinal to H), 25.6 (β-CH_2 vicinal to Cl), 26.6 and 23.7 (β-CH_2 vicinal to H). Compounds **9–12** gave satisfactory elemental analyses and were characterized by mass spectrometry.