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Unexpected Reaction of 2,5-Dichloro-1,4-benzoquinone with Pyrrolidine

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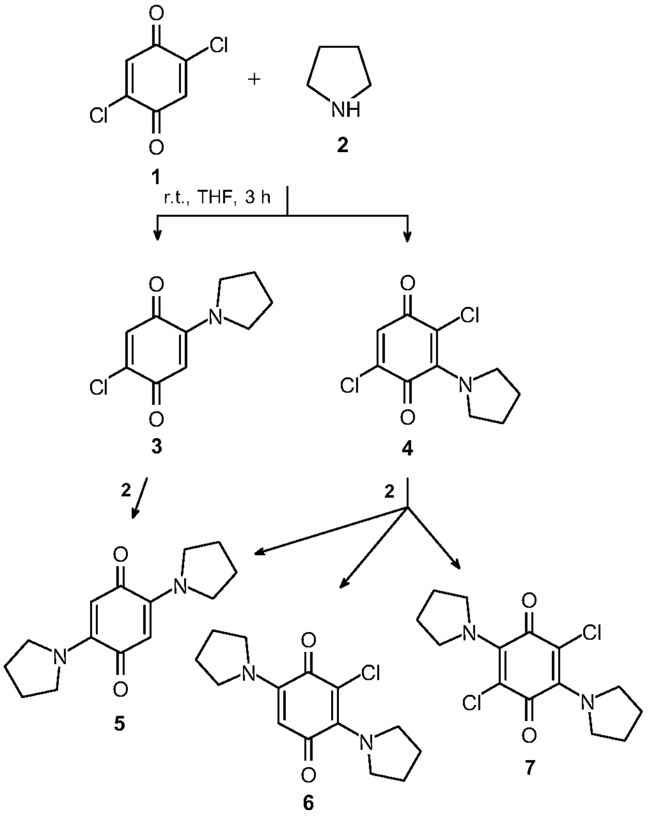
2,5-Bis(pyrrolidino)-3-chloro-1,4-benzoquinone has been shown to be unexpectedly the major product in the reaction of 2,5-dichloro-1,4-benzoquinone with pyrrolidine.

The nucleophilic substitution of chloro-1,4-benzoquinones (CBQ) is of considerable interest and has been extensively studied.[1] 2,5-Dichloro-1,4-benzoquinone **1** has been shown to give in reactions with amines either the products of nucleophilic replacement of two chlorine atoms by amine at positions 2 and 5 or the products of reductive addition of two molecules of amine to positions 3 and 6.[2] We have found no examples in the literature of any other direction of the reactions of **1** with amines except those mentioned above.

On investigating the reaction of **1** with pyrrolidine **2** we have found that in contrast to the expected bisaminoquinones **5** and **7**, the major product of the reaction was, surprisingly, quinone **6**.[†] The same quinone **6** has been recently reported[3] to be the main product in the reaction of 2,6-dichloro-1,4-benzoquinone with pyrrolidine. The alteration of the reaction conditions (temperature, pressure, solvent) did not affect appreciably the yield of **6** which was 34–38%, independent of the reaction conditions. However, when the reaction was carried out with a deficit of **2** (molar ratio of amine:quinone, 1:2) two new compounds were obtained as the main products along with starting **1** (70%) and traces of final **6** ($<2\%$). The elemental analysis and spectroscopic data[‡] show two new products to be monoaminoquinones **3** and **4** in 16% and 10% yields, respectively.

As expected, the reaction of **3** with an excess of **2** gave **5** in 95% yield. On the other hand, the reaction of **4** with **2** gave, surprisingly, all three bisaminoquinones **5**, **6** and **7** in 2%, 90% and 2% yields, respectively. Similar complex transformations of quinones upon the action of aliphatic amines have been found earlier for some other reactions.[4,5] Another example of such unusual reactions is the replacement of the methyl group in quinones by aliphatic amines, the mechanism of which still remains unclear.[6] It is interesting to note that in all the above-mentioned reactions[5,6] unexpected results were observed as usual at the stage of amination of monoaminoquinones. Although the chemistry of monoaminoquinones remains practically unexplored to date it is known that some monoaminoquinones can undergo spontaneous disproportionation to the corresponding 2,5-bisamino derivatives.[7] The very high yields (90%) in these reactions indicate that such disproportionation most likely involves non-photochemical [2 + 2]-biscycloaddition and cycloreversion of two monoaminated quinone molecules. As usual, the facile non-photochemical [2 + 2]-cycloaddition is typical of systems which react *via* intermediate EDA complexes, zwitterions or biradicals, and the best results are obtained in reactions in which the electron-rich olefins contain amino groups.[8] Recently we have shown that the presence of an extremely strong electron-donating pyrrolidine group and several electron-withdrawing chlorine atoms in quinones results in a pronounced tendency of these compounds to form EDA complexes due to their self-complexation.[3] In the UV-VIS spectra these compounds display a broad and rather intensive absorption band in the region of 400–700 nm. A similar broad absorption band with its peak at 555 nm ($\varepsilon = 3000$) is also observed for quinone **4**. By analogy with the disproportionation of monoaminoquinones,[7] it seems reasonable to propose that the reaction of **4** with **2** also involves [2 + 2]-biscycloaddition and cycloreversion (Scheme 2). The initiation of such a process could be an electron-transfer stage from the amine to the LUMO of quinone **4**, this being the first step in the reactions of quinones with amines.[9] Although the data obtained do not allow us to discuss in detail all the peculiarities of the mechanism proposed, the literature data for the less conjugated methylquinones show that such reactions proceed *via* cage intermediates such as **14** and **15**.[10] The replacement of the bridgehead chlorine atoms in such cage intermediates most probably proceeds *via* an $S_{RN}1$ mechanism[11] in which the most reactive position should be the one adjacent to the pyrrolidino group. Due to unfavourable steric and electronic effects[12] both N–C–C–N bonds in cage intermediates **14** and **15** should be unstable and break up to give final quinones **5**–**7**. The predominant formation of **6** in this reaction is in good agreement with the data from X-ray analysis, showing that quinone coupling gives as usual less sterically hindered couples such as **8**[13] which can be additionally stabilized by Cl···Cl contacts.[14]



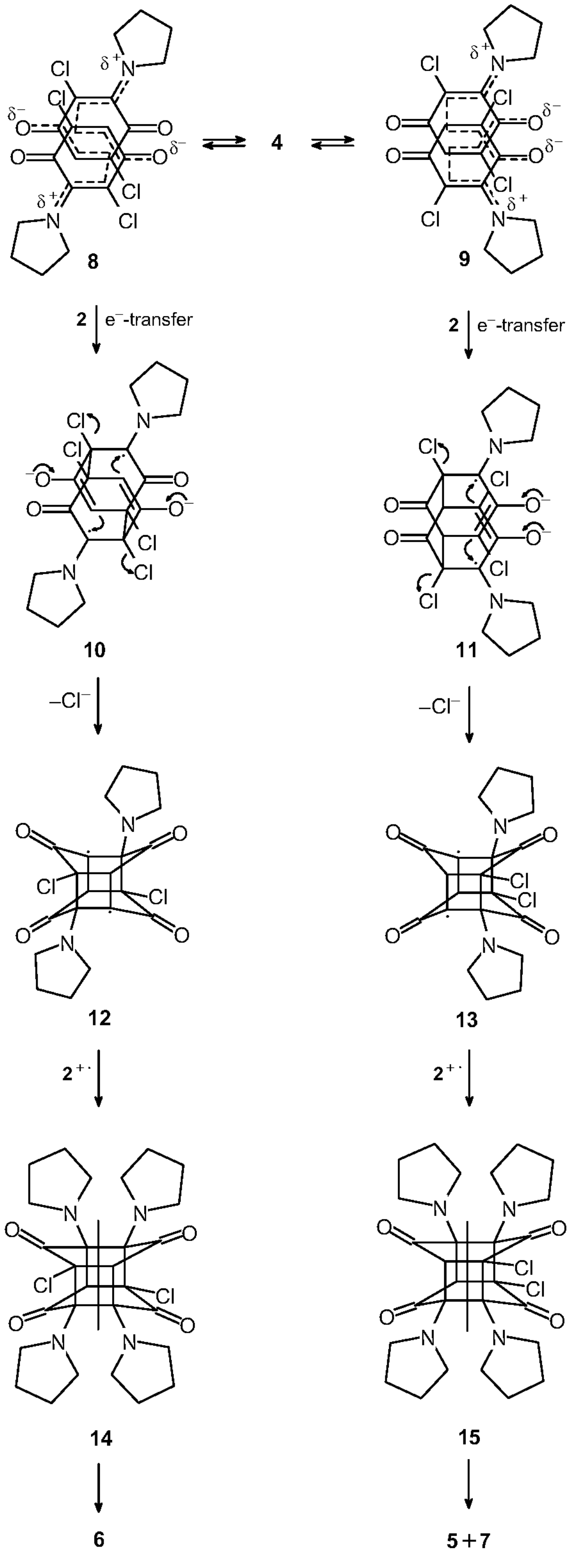
Scheme 1

It is worth mentioning that although the formation of **6** in the reaction of **4** with **2** can also be explained by the *cine*-substitution of the chlorine in **4** by amine (AE_a mechanism),[15] such an approach is of no use in accounting for the formation of **5** from **4**. Moreover, the formation of **7** from **4** by the mechanism of reductive addition[1] seems also to be very unlikely, taking into account the more negative value of the half-wave potential of monoaminoquinones with respect to the corresponding 2,5-bisamino derivatives.[16] On the other hand, the mechanism proposed here allows us to explain not only the formation of **5**–**7** from **4** but also that of 2,5-bis(butylamino)-3-methyl-1,4-benzoquinone in the amination of 2-butylamino-5-methyl-1,4-benzoquinone.[5]

[†] *Reaction procedure.* Pyrrolidine (284 mg, 4.0 mmol) was added under a nitrogen atmosphere at room temperature in the dark to a stirred solution of **1** (177 mg, 1.0 mmol) in dry THF (50 ml). After 3 h of stirring the solvent was evaporated under reduced pressure and the residue was chromatographed on a column with silica gel using hexane–ethyl acetate (1:1) as eluent. Three products were obtained: **5**, 79 mg (32%); **6**, 50 mg (36%); and **7**, 21 mg (20%); dense red microcrystals (from benzene–ethyl acetate); m.p. 178–180 °C (decomp.); UV-VIS (CH_2Cl_2) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 546 (960), 393 (19200), 303 (12800), 228 (13800); IR ν_{max}/cm^{-1} 2967, 2949, 2875 (C–H), 1631 (C=O), 1533 (C=C); ^{1}H NMR ($CDCl_3$) δ 3.96 (m, 8H, α-CH_2), 1.90 (m, 8H, β-CH_2); ^{13}C NMR ($CDCl_3$) δ 175.1 (C-1), 149.9 (C-2), 101.5 (C-3), 54.4 (α-CH_2), 25.6 (β-CH_2). Compound **7** gave satisfactory elemental analyses and was characterised by mass spectroscopy.

The reaction of 2,6-dichloro-1,4-benzoquinone (177 mg, 1.0 mmol) with pyrrolidine (284 mg, 4.0 mmol) was carried out in a similar manner as described above. Two products were obtained: **6**, 87 mg (62%) and **5**, 7 mg (3%). Characteristic data for compounds **5** and **6** are given in ref. 3.

[‡] Characteristic data for compound **3** are given in ref. 3. **4**: dense violet needles (from pentane–ethyl acetate); m.p. 86.5–87.5 °C (decomp.); UV-VIS (CH_2Cl_2) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 555 (3000), 298sh (7700), 264 (15600), 247sh (13800); IR ν_{max}/cm^{-1} 3046, 2957, 2927, 2878 (C-H), 1690, 1630 (C=O), 1600, 1523 (C=C); ^{1}H NMR ($CDCl_3$) δ 7.03 (s, 1H, arom-H), 3.92 (m, 4H, α-CH_2), 1.93 (m, 4H, β-CH_2); ^{13}C NMR ($CDCl_3$) δ 177.5 (C-4), 176.7 (C-1), 146.4 (C-3), 138.7 (C-5), 134.1 (C-6), 109.2 (C-2), 54.3 (α-CH_2), 25.7 (β-CH_2). Compound **4** gave satisfactory elemental analyses and was characterised by mass spectroscopy.



Scheme 2

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References

1 K. T. Finley, *The Chemistry of the Quinonoid Compounds,* ed. S. Patai, Wiley, Interscience Publication, London, 1974, Part 2, pp. 877–1144.

2 R. A. Henry and W. M. Dean, *J. Am. Chem. Soc.*, 1952, **74**, 278; D. Buckley, H. B. Henbest and P. Slage, *J. Chem. Soc.*, 1957, 4891.

3 S. V. Chapyshev and T. Ibata, *Mendeleev Commun.*, 1994, 109.

4 A. Ya. Berlin and A. N. Makarova, *Zh. Obshch. Khim.*, 1960, **30**, 1380 [*J. Gen. Chem. USSR (Engl. Transl.)*, 1960, **30**, 1380].

5 J. Kumanotani, F. Kagawa, A. Nikosawa and K. Sugita, *Bull. Chem. Soc. Jpn.*, 1968, **41**, 2118.

6 J. Hoffman, *Chem. Ber.*, 1901, **34**, 1558; O. Böters, *Chem. Ber.*, 1902, **35**, 1502; W. K. Anslow and H. Raistrick, *J. Chem. Soc.*, 1939, 1446; D. W. Cameron and P. M. Scott, *J. Chem. Soc.*, 1964, 5569; D. W. Cameron, R. G. F. Giles and R. B. Titman, *J. Chem. Soc. (C)*, 1969, 1245.

7 C. J. Cavallito, A. E. Soria and J. O. Hoppe, *J. Am. Chem. Soc.*, 1950, **72**, 2661.

8 T. Gotoh, A. B. Padias and H. K. Jr. Hall, *J. Am. Chem. Soc.*, 1986, **108**, 4920.

9 T. Yamaoka and S. Nagakura, *Bull. Chem. Soc. Jpn.*, 1971, **44**, 2971.

10 H. Hopf and H. Musso, *Chem. Ber.*, 1973, **106**, 143.

11 I. P. Beletskaya and V. N. Drozd, *Usp. Khim.*, 1979, **48**, 793 (*Russ. Chem. Rev.*, 1979, **48**, 793).

12 S. Dähne and F. Moldenhauser, *Progress in Physical Organic Chemistry*, ed. R. W. Taft, Wiley, New York, 1985, vol. 15, pp. 1–130.

13 D. Rabinovich, *J. Chem. Soc. (B)*, 1967, 989.

14 J. Bernstein, M. D. Cohen and L. Leiserwitz, *The Chemistry of the Quinonoid Compounds*, ed. S. Patai, Wiley, Interscience Publication, London, 1974, Part 1, pp. 104–105.

15 T. Kauffmann, R. Nürnberg and K. Udluft, *Angew. Chem., Int. Ed. Engl.*, 1968, **7**, 617.

16 D. W. Cameron, R.G.F.Giles and M. H. Pay, *Tetrahedron Lett.*, 1970, 2049.

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