A new approach to the synthesis of 2,5-bis(alkylamino)-1,4-benzoquinones by the reaction of DDQ with aliphatic amines

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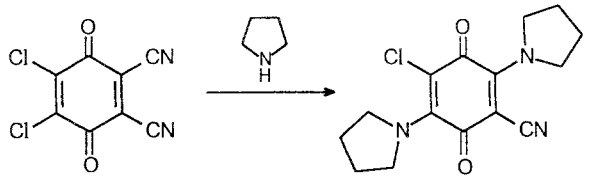
2,5-Bis(alkylamino)-1,4-benzoquinones (BAQ) belong to the class of strongly-conjugated merocyanine compounds, which are characterized by extremely high polarizability of the n,p-electron system, and, as a result, by a number of interesting chemical and physical properties.[1] The general method of the synthesis of BAQ is known to be the reactions of quinones with aliphatic amines.[2] Nevertheless, the reactions of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) with amines have remained unexplored and the application of DDQ in organic synthesis has been limited only to its well-known role as a convenient oxidizing reagent.[3] In the study of the reaction of DDQ (**1**) with pyrrolidine we found that along with nucleophilic substitution of the chlorine atom at position 2 DDQ undergoes nucleophilic substitution of the cyano group at position 5 to give quinone **2** as the sole product in 56 % yield.



1 **2**

The presence of the cyano group in quinone **2** leads to an additional increase in the conjugation of the pyrrolidino groups with the quinone nucleus, which results in the most pronounced merocyanine properties of this compound among all previously known BAQ.[1] Thus, quinone **2** exhibits paramagnetic properties, which were known earlier only for some strongly-conjugated polyaminoquinones that are of interest in the preparation of new photo- and semi- conductive organic materials.[4] Preparation of BAQ by the reaction of DDQ with aliphatic amines may be a promising method for the synthesis of new strongly-conjugated quinones, which could possess a set of useful chemical and physical properties.

3-Chloro-6-cyano-2,5-bis(pyrrolidino)-1,4-benzoquinone (2), m.p. > 350 °C. IR (KBr, ν/cm^{-1}): 2975, 2950, 2930, 2872 (C—H), 2203 (C≡N), 1630 (C=O), 1541, 1525 (C=C). NMR ^1H (CD_3Cl), δ: 4.15 (br.s, 2 H, NCH_2); 4.06 (br.s, 2 H, NCH_2); 3.98 (br.s, 4 H, NCH_2); 2.00 (br.s, 4 H, CH_2); 3.98 (br.s, 4 H, CH_2). NMR ^{13}C ($CDCl_3$), δ: 178.2 (C-1); 172.7 (C-4), 153.9 (C-5); 149.8 (C-2); 116.9 (C≡N); 104.9 (C-3); 82.1 (C-6); 54.6, and 54.5 (NCH_2); 25.7, 25.4, and 24.5 (CH_2). Found (%): C, 58.94; H, 5.23. $C_{15}H_{16}ClN_3O_2$. Calculated (%): C, 58.88; H, 5.27.

References

1. S. Dahne and F. Moldenhauser, *Progress in Physical Organic Chemistry*, Ed. R. W.Taft, Wiley, New York, 1985, **15**, 1.
2. K. T. Finley, in *The Chemistry of the Quinonoid Compounds*, Ed. S. Patai, Wiley, London, 1974, Part 2, 877.
3. D. Walker and J. D. Hiebert, *Chem. Rev.*, 1967, **67**, 153.
4. A. S. Lindsay, in *The Chemistry of the Quinonoid Compounds*, Ed. S. Patai, Wiley, London, 1974, Part 2, 793.

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