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GENERATION AND TRAPPING OF 2,3-NAPHTHOQUINONE

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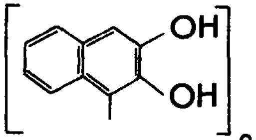
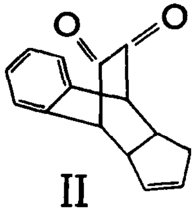
Abstract: 2,3-Naphthoquinone generated from 2,3-dihydroxynaphthalene was trapped with cyclopentadiene and its properties examined by dc polarography and cyclic voltametry.

2,3-Naphthoquinone is one of the three missing members in the family of naphthoquinones. Up to the present all attempts of preparation failed and older claims of a successful synthesis were corrected later.[1] The study of the oxidation of 2,3-dihydroxynaphthalene with Co^{3+} followed potentiometrically indicated instability for the primary oxidation product, apparently the 2,3-napthoquinone. The spontaneous chemical transformation of the latter was characterized as polymerization.[2] The only physicochemical information which characterizes 2,3-naphthoquinone is the polarographic halfwave potential reported by Horner;[3] however, it is of no value for structural characterization as will be shown later. Even the structurally related 1,4-diphenyl-2,3-naphthoquinone generated from the respective dihydroxy compound did not prove higher stability. Depending on the experimental conditions, the isolated product was either a trimer or, in the presence of butadiene, a Diels-Alder adduct.[4] In this paper the results of our recent studies of the chemical and electrochemical oxidation of 2,3-dihydroxynaphthalene are reported.

The oxidation of 2,3-dihydroxynaphthalene with aqueous KIO_3 and, eventually, in the presence of solvents such as methanol, acetone, and ethyl acetate in a single or two-phase system, produced either a 1,1'-dimer (I) already reported in the literature[5] or a polymer. The structure of the latter has not yet been fully characterized. The 1;1'-dimer (I) was also the exclusive product of an oxidation in the presence of cyclopentadiene in a mixture of water with organic solvent, e.g., methanol, acetone, ethyl acetate. However, from the oxidation of 2,3-dihydroxynaphthalene with aqueous KIO_3in the presence of a large excess of cyclopentadiene (as a separate phase, in the absence of organic solvents), besides a small quantity of 1,1'-dimer, a yellow compound was isolated in 56% yield and identified as compound II, m.p. 170° after crystallization from cyclohexane and vacuum sublimation.



I



II

Its IR spectrum (KBr pellet) showed a strong absorption at 1730 cm^{-1}, NMR spectrum ($CDCl_3$) absorptions at 7.1 - 7.4 δ (m, 4H), 5.3 δ (m, 2H), 4.0 - 4.1 δ (d, 1H), 3.8 - 3.9 δ (d, 1H), 3.5 δ (d, 1H), 2.8 - 3.1 δ (m, 1H), 2.4 - 2.6 δ (m, 1H), 2.1 - 2.2 δ (s, 1H), and MS fragmentation 224 M^+ (100%), 196 (18.7%), 188 (20.7%), 166 (18.7%), 160 (18%), 146 (65.3%), 132 (6.7%), and 104 (48%). The reduction of II with $NaBH_4$ yielded a diol, m.p. 160° (from cyclohexane), characterized with a strong IR band at 3200 - 3600 cm^{-1}. The oxidation with H_2O_2 in the presence of NaOH gave a diacid, m.p. 253°C, characterized in the IR spectrum with a broad band at 2500 - 3200 cm^{-1} and a strong band at 1690 cm^{-1}.

Trapping of 2,3-naphthoquinone as a Diels-Alder adduct is the first evidence of the existence of this unstable species. The cycloaddition is enabled by favorable energies of both the LUMO of 2,3-naphthoquinone[6], acting as acceptor, and the HOMO value of cyclopentadiene acting as a donor. Furthermore, a low-lying triplet is another factor contributing to the exceptionally high reactivity of the former molecule.

In order to obtain a better understanding of the behavior of 2,3-naphthoquinone in aqueous medium, anodic oxidation of 2,3-dihydroxynaphthalene was examined by dc polarography and cyclic voltametry. The wave observed in borate buffers with dc polarography at DME from pH 8.8 to 9.5 [$E_{1/2}$ -0.39 to -0.46 V vs a Hg/1M Hg_2SO_4 electrode] showed nonfaradaic adsorption electrode mechanisms. The mechanism disqualifies the $E_{1/2}$ value reported by us (and by Horner as well) from any practical use for structural correlations. Cyclic voltametry in different aqueous buffers using a graphite paste electrode and a sweep rate of 0.16 V/s showed an anodic peak only [in acetate buffer pH 4.0, Ep = +0.72 V vs SCE] indicating a rapid depletion of the electrode surface of 2,3-naphthoquinone. This behavior is explained by a rapid dimerization or polymerization of the quinone. Repeated scanning resulted in a systematic decrease of the peak height to 15% of the original peak height indicating contamination of the electrode surface with the final reaction products (dimer, polymer). This behavior is in complete agreement with the previously reported instability of 2,3-naphthoquinone using the potentiometric method (vide supra).

References and Notes

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