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Dimethyldioxirane Oxidation of Hydroquinones into Quinones and 2,3-Dihydroxycyclohexene-1,4-diones

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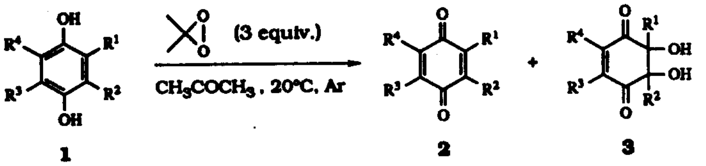
Key words: Dioxirane, hydroquinones, cyclohexene-1,4-dione-2,3-diols, electron transfer, oxygen transfer

Abstract: *Dehydrogenation of hydroquinones 1 by dimethyldioxirane affords quinones 2 and oxygen transfer the novel 2,3- dihydroxycyclohexene-1,4-diones 3 ; an electron transfer mechanism is proposed for these oxidations.*

Two recent publications [1] on the oxidation of phenols, catechols and hydroquinones by dioxiranes [2] prompt us to communicate our preliminary results. The surprising feature under our conditions is that the hydroquinone 1 gave, besides the expected quinones 2 , the unusual 2,3-dihydroxycyclohexene-1,4-diones 3 (Eq. 1), in case 1b even as major product (Table 1). In fact, it is likely that the hydroxyquinones 15 (cf. Ref. 1a) and 7 (cf. Ref. 1b) are dehydration products of the respective dihydroxy derivatives 3. These enedione-diols 3 are accessible through the direct *cis*- dihydroxylation of quinones by osmium tetroxide [3], but have so far received little attention for synthetic purposes.



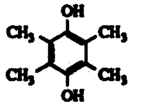
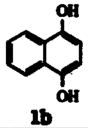
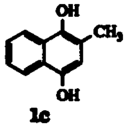
(Eq.1)

In analogy to other peroxides, also for dioxiranes have electron transfer (ET) processes been proposed [4]. Hydroquinones, which are important antioxidants of biological significance and their redox chemistry has been well investigated[5], should be convenient electron donors to explore the ET chemistry of dimethyldioxirane.

Since the oxidation of the hydroquinones to the corresponding quinones is effected by benzoyl peroxides, whose mechanism has been recently [6] examined in detail and involves a succession of electron and proton transfer steps [7], we expected analogous redox behavior for dimethyldioxirane. Presently we report our preliminary results on the oxidation of methyl-substituted and benzo-annelated hydroquinones and confirm the production of the corresponding quinones by dehydrogenation. However, for preparative purposes more significant, we obtained the hitherto little known [3] 2,3-dihydroxycyclohexene-1,4-diones as side products through oxygen transfer chemistry by dimethyldioxirane.

The hydroquinones **1** were treated with a three-fold molar excess of dimethyldioxirane in acetone solution at room temperature under argon gas atmosphere to afford the oxidation products in Eq.1. After evaporation of the solvent, the quinones **2** and the 2,3-dihydroxycyclohexene-1,4-diones **3** were isolated by column chromatography on silica gel. The yields are listed in Table 1.

Table 1: Reaction of dimethyldioxirane with hydroquinones.

substrate	 **1a**	 **1b**	 **1c**
reaction time [h][a)]	1.5	24	24
yield of **2** [%][b)]	87	34	61
yield of **3** [%][b)]	13	66	39
mass balance [%]	83	78	73
ratio of diastereomers	-	80 : 20	80 : 20

a) complete conversion of **1**; b) isolated by column chromatography on silica gel, normalized to 100%

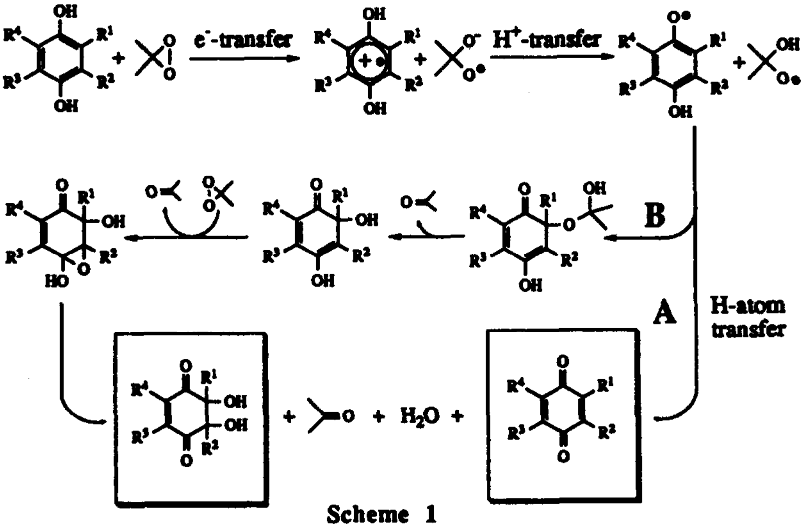
The identification of the quinones **2** was made by comparison of their spectra, melting points, and TLC retention times with the authentic materials, while the characterization of the novel oxidation products **3a-c** rests on ^{1}H and ^{13}C NMR and IR spectral data [8]. Furthermore, for the known **3b** the spectral data and melting point were in accordance with those reported [3]. Diol **3b** was accompanied by its known [9], orange-colored oxidation product, the 2,3-dihydroxy-1,4-naphthoquinone (mp 275-277 °C, lit. [9] mp 280-281°C).

The naphthalene derivatives **3b,c** were obtained as diastereomeric mixtures, presumably *cis/trans* isomers, easily recognized by ^{1}H NMR. Unfortunately, it has so far not been possible to separate these diastereomers by chromatographic techniques, so that their configurations could as yet not be determined.

Furthermore, by NMR spectral means it was not possible to establish whether the only isolated diastereomer of **3a** has the *cis* or *trans* stereochemistry.

It is worth mentioning that quinone epoxides could not be detected in the ^1H NMR spectra of the product mixtures of all the hydroquinones **1** studied here. Control experiments confirmed that the quinones **2** are resistent towards epoxidation by dimethyldioxirane under the conditions employed for the hydroquinones **1**. Only under prolonged reaction times, elevated temperatures, and large excess of dioxirane, could in the case of naphthoquinone **2b** small amounts of its epoxide be observed by NMR spectroscopy (unpublished results, L. Hadjiarapoglou).

In view of the established redox chemistry of hydroquinones [7], we postulate for the mechanism of the dehydrogenation of the hydroquinones to the quinones by dioxirane the ET process shown in pathway **A** of Scheme 1. For the formation of the dihydroxy-enediones **3** we propose the oxygen transfer steps along pathway **B** in Scheme 1.



Scheme 1

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8. Spectral data and physical constants of **3a-c** (major / minor diastereomer): **3a**, colorless needles, mp 87-89 °C; ^{1}H NMR ($CDCl_3$, 250 MHz): δ= 1.34 (s, 6H, 2,3-CH_3), 2.07 (s, 6H, 5,6-CH_3), 3.47 (s, 2H, 2,3-OH, exchanged with D_2O).- ^{13}C NMR ($CDCl_3$, 63 MHz): δ= 13.2 (q, 2,3-CH_3), 20.0 (q, 5,6-CH_3), 80.6 (s, 2,3-C), 143.5 (s, 5,6-C), 198.7 (s, 1,4-C).- IR ($CDCl_3$): ν= 3520 cm^{-1}, 2975, 1703, 1630.- **3b**, pale yellow needles, mp 165-168°C; lit.[7] mp 170-172 °C.- ^{1}H NMR ([D_6]-acetone, 250 MHz): δ= 4.82/4.70 (s, 2H, 2,3-H), 7.89/7.80 (dd, J=3Hz, 2H, 6,7-H), 8.04/8.02 (dd, J=3 Hz, 2H, 5,8-H).- ^{13}C NMR ([D_6]-acetone, 63 MHz): δ= 78.2/79.3 (d, 2,3-C),126.5-135.3 (4´,5,6,7,8,8´-C), 196.7/193.2 (s, 1,4-C).- IR (CH_2Cl_2): ν= 3700 cm^{-1}, 3500, 2940, 1725, 1650, 1600.- **3c**, colorless needles, mp 155-158°C.- ^{1}H NMR ([D_6]-acetone, 250 MHz): δ= 1.55/1.30 (s, 3H, 2-CH_3), 4.60/4.72 (s, 1H, H-3), 7.87 (dd, J=3 Hz, 2H, 6,7-H), 8.04 (dd, J=3 Hz, 5,8-H).- ^{13}C NMR ([D_6]-acetone, 63 MHz): δ= 20.1 (q, 2-CH_3), 80.4 (s, 2-C), 80.8 (d, 3-C), 127.0-135.2 (4´,5,6,7,8,8´- C), 196.8/196.3 (s, 1,4-C).- IR (CH_2Cl_2): ν= 3695cm^{-1}, 3520, 2940, 1710, 1600.-
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