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NONSELECTIVE DISPROPORTIONATION OF ISOMERIC HYDROXYCYCLOHEXADIENYL RADICALS TO PHENOLS[1]

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Comparison of the isomer ratios and yields of cresol, methoxyphenol, and nitrophenol, which were obtained by the aromatic hydroxylation with hydroxyl radical in the presence or absence of benzoquinones in anhydrous media, indicates that disproportionation of hydroxycyclohexadienyl radicals occurs nonselectively.

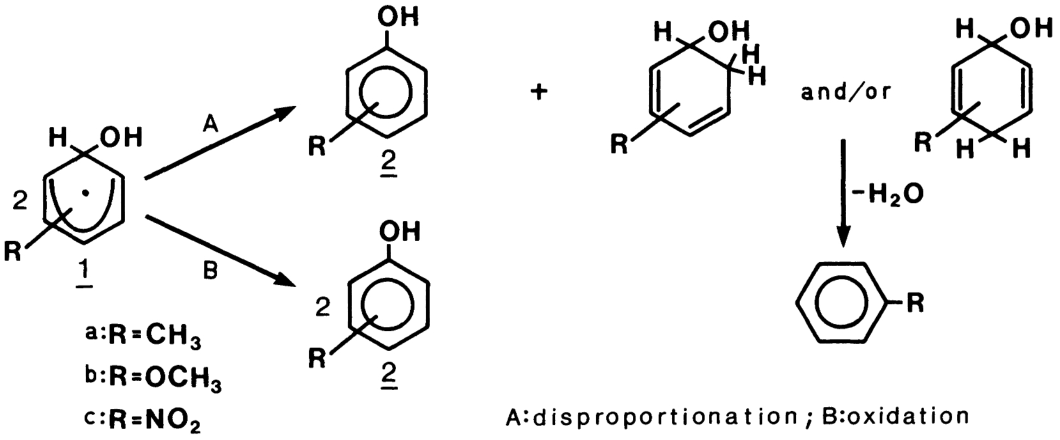
The aromatic hydroxylation with hydroxyl radical proceeds through hydroxycyclohexadienyl radical intermediates (1). In the absence of oxidants, isomeric hydroxycyclohexadienyl radicals (1) disproportionate to give phenols (Scheme 1-A). It has long been an unanswered question, however, whether the disproportionation between ortho, meta, and para-oriented isomers of 1 occurs selectively or nonselectively.[2,3] If the disproportionation of 1 is nonselective, the isomer ratio of phenols (2) resulting from the aromatic hydroxylation reflects the correct distribution ratio of the positional isomers of 1. If the disproportionation is selective, the isomer ratio of phenols reflects the selectivity of the disproportionation. In the presence of effective oxidants, on the other hand, isomeric radicals (1) are converted to phenols efficiently, and the isomer ratio of phenols truly reflects the ratio of the isomer distribution in 1 (Scheme 1-B).[2,3]

Therefore, it is predicted that if the disproportionation of 1 is nonselective, the isomer ratio of phenols resulting from the aromatic hydroxylation with hydroxyl radical in the absence of oxidants is the same as that in the presence of the oxidants. In this case, at the same time, the yields of phenols is more than doubled in the presence of the oxidants as compared with yields in the absence of the oxidants (see Scheme 1). This relation of the isomer ratio and yield of phenols will not be held if the disproportionation of 1 is selective.

In order to test this hypothesis, we carried out the aromatic hydroxylation in anhydrous media by using α-azobenzyl hydroperoxide (3) as a hydroxyl radical source,4) and benzoquinones as oxidants for 1.5) In this way, the mechanistic complexity arising from the formation of radical cation (4)6) from 1 due to dehydration can be avoided. Benzoquinones are known to be an efficient oxidant for 1b ($k_{ox} = 10^7 - 10^9 M^{-1}s^{-1}$).5) Molecular oxygen is not a good oxidant for the purpose of the present study, because it is incorporated into phenols.7)

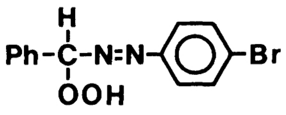
Photodecomposition of 3 in toluene, anisole, or nitrobenzene (10^{-2}M) with a high pressure mercury lamp through a Pyrex filter under argon gas in the presence or absence of p-benzoquinone gave cresol, methoxyphenol, or nitrophenol respectively.4) The yields and ortho:meta:para isomer ratios of the above menthioned phenols are indicated in Table 1. The hydroxylation of toluene with 3 was also carried out in the presence of 2-methylbenzoquinone or 2,5-di-tert-butylbenzoquinone, by using a high pressure mercury lamp with a Corning glass filter 5-60.8) Similar results of the yield and isomer ratio of cresol were obtained.

From comparison of the data in Table 1, the following important points can be deduced:



A:disproportionation ; B:oxidation

Scheme 1.



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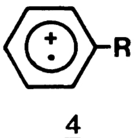

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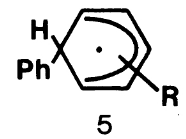

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Table 1. Isomer ratio and yield of phenols in the presence or absence of p-benzoquinone[a,b]

Phenols (2) Quinone[c]	R=CH_3 o : m : p	%[a]	R=OCH_3 o : m : p	%[a]	R=NO_2 o : m : p	%[a]
nil	71: 9 :20	8	84: –[d]:16	14	26:48:26	16
0.02 M	69:11:20	22	80: –[d]:20	43	29:44:27	14
0.05 M	73:11:16	25	80: 2 :18	51	29:46:25	14
0.10 M	72:12:16	27	81: –[d]:19	40	29:40:31	13

a) Yields are based on original amount of 3.
b) Data were obtained by repeating the experiment several times.
c) Concentration of p-benzoquinone in aromatics.
d) Only a trace of m-methoxyphenol was detected by GLC.

(i) The isomer ratios of cresols and methoxyphenols showed nearly constant values regardless of the presence or absence of the oxidant (p-benzoquinone).

(ii) The yields of both cresol and methoxyphenol more than doubled in the presence of the oxidant as compared with those in the absence of it.

(iii) The yield of nitrophenol did not increase even in the presence of a large excess of p-benzoquinone, while the isomer ratio showed a constant value within experimental error.

(iv) The average values of the ortho:meta:para isomer ratios of cresols, methoxyphenols, and nitrophenols are 71:11:18, 81:1:18, and 28:45:27, respectively, which are consistent with results reported by us previously.[9]

The different oxidation effects of p-benzoquinone on the yields of those phenols (see ii and iii) can be explained as follows. Both 1a and 1b possess a higher SOMO energy[10] (-8.5 — -8.9 eV) as compared with 1c (-9.8 — -10 eV), and they (1a and 1b) can be oxidized by the quinone probably via electron transfer interaction between their SOMO's and the quinone. This type of interaction, however, is not feasible for 1c which has a low SOMO.

The yield and isomer ratio of cresol, for example, were not affected by the concentration of 3 (10^{-1} - 10^{-4}M), implying that 3 itself is not an oxidant for 1. Similarly, p-bromophenyl radical which is formed from 3 together with hydroxyl radical by photodecomposition, is not an oxidant for 1.[4,11] The relation between the yields and isomer ratios of cresol and methoxyphenol as indicated by i and ii agrees well with the prediction for the nonselective disproportionation. Therefore, all our present observations strongly support the nonselective disproportionation of 1.

The following is worth noting. It seems that there was a trend for the ratio of m-cresol to increase slightly, while that of p-cresol decreased, when the concentration of the quinone was increased (see Table 1). One can regard this as an indication that 1a receives selective disproportionation in which the meta-oriented isomer of 1a is reduced by the para-oriented isomer. This would give a slightly lower ratio for m-cresol and higher ratio for p-cresol at a low concentration of the quinone. However, the observed change of the isomer ratio of those cresols is very small and probably lies within experimental error. Therefore, we consider that the contribution of the selective disproportionation is only minor even if it does compete with the nonselective disproportionation.

In summary, the present studies provide, for the first time, evidence for the nonselective disproportionation of 1. It is also worthy to note that Eberhardt et al. suggested, on the basis of the radiolysis data, that the disproportionation of 1 is selective.[2)] On the other hand, the disproportionation of phenylcyclohexadienyl radicals (5) is reported to be nonselective.[12)] Our present observations are consistent with the conclusion obtained for 5.

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8) Under this condition, the longest absorption band of 3 (410 nm) is excited selectively.
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10) The values were calculated by CNDO/2.
11) p-Brompphenyl radical adds efficiently to benzene, for example, to give p-bromodiphenyl in a high yield.
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