

The Hydroxylation of Phenols by the Photolysis of Hydrogen Peroxide in Aqueous Media

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DIRECT hydroxylation of aromatic compounds has been studied by many workers.¹ For example, phenol is hydroxylated to catechol and hydroquinone with the free hydroxyl radical generated by the metal ion-catalyzed decomposition of hydrogen peroxide (*e.g.*, Fenton's reagent) or by X-irradiation of water. In general the yield of the products is low, due to either the complication by side-reactions or the slow reaction rate. Recently the hydroxyl radical produced by ultraviolet^{2,3} or visible-light⁴ (in the presence of a sensitizer)

irradiation of hydrogen peroxide has been applied to the hydroxylation of aromatic compounds (*e.g.*, benzene, anisole, and fluorobenzene).

We report here that the photolysis of hydrogen peroxide in the presence of a phenol in aqueous solution results in the formation of polyhydroxylated phenols in moderate yields. In a typical run, a solution of *p*-cresol (4 g.) and hydrogen peroxide (~ 1.0 g.) in water (230 ml.) was irradiated for nine hours with a low-pressure mercury lamp under nitrogen. After the photolysis, the remaining

hydrogen peroxide was decomposed with sodium hydrogen sulphite. Vapour-phase-chromatographic analysis of the volatile product showed that this consisted only of the starting material (0.52 g.) and 3,4-dihydroxytoluene (0.80 g.). The procedure was applied to a number of water-soluble phenols. The results are summarized in the Table.

The hydroxylation occurs in the *ortho*- and *para*-positions to the hydroxyl group of the phenols, and the *ortho*-hydroxylation seems to be preferential.

This is in contrast to the case of the Elbs persulphate oxidation in which *para*-hydroxylation is predominant.⁵ In the cases of *p*-cresol and phloretic acid, only an *ortho*-hydroxylated derivative was obtained. Thus this method may be used for the synthesis of catechol derivatives from some *p*-substituted phenols. Studies on the scope of this reaction and on the application to the hydroxylation of other phenols, including natural phenolic compounds, are now in progress.

TABLE

Starting phenol				Irradiation time (hr.)	Recovered phenol (%)	Yields of the products (%)*
Phenol	6	22	Catechol (26), hydroquinone (14), pyrogallol (5), 1,2,4-trihydroxybenzene (trace)
<i>p</i> -Cresol	9	13	3,4-Dihydroxytoluene (20)
Catechol	5.7	35	Pyrogallol (22), 1,2,4-trihydroxybenzene (3)
Hydroquinone	5	33	1,2,4-Trihydroxybenzene (6)
Phloretic acid	6.5	20	3,4-Dihydroxyphenylpropionic acid (28)

* Yields are based on the consumed starting material.

(Received, January 31st, 1966; Com. 056.)

¹ Cf., for example, J. D. Loudon, *Progr. Org. Chem.*, 1961, 5, 46, and R. Stewart, "Oxidation Mechanism; Applications to Organic Chemistry", W. A. Benjamin, New York, 1964.

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⁴ J. R. Williams, Jr., and R. H. Steele, *Biochemistry*, 1965, 4, 814.

⁵ J. Forrest and V. Petrow, *J. Chem. Soc.*, 1950, 2340.