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OXIDATION OF AROMATIC SUBSTRATES WITH HYDROGEN PEROXIDE AND HYDROCHLORIC ACID

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Abstract: Chloroquinones are prepared conveniently from phenol, naphthols and aromatic amines.

Oxidation of aromatic substrates with hydrogen peroxide has been studied under a variety of conditions[1-6]. Acidity of the medium and presence of metal salts[5,6] have profound influence in determining the reactive species involved in the course of the reaction. Atleast three different species have been implicated under different conditions, viz. $^{\bullet}OH$[1], $^{\bullet}O-OH$[7] ^{+}OH[3,4].

With hydrogen peroxide and mineral acids like sulphuric acid[8], phenols give either polymeric materials or ring cleaved products[9]. We have observed that using hydrochloric acid and excess of hydrogen peroxide results in a convenient conversion of phenols and aromatic amines to chloroquinones, in good yields in a number of cases (Table 1).

The formation of chloroquinone takes place presumably through the prior formation of chlorophenols or their analogues. In view of the varied synthetic applications of chloroquinones and also their facile convertability to the parent quinones, formation of chloroquinones is of synthetic interest.

Experimental procedure

To 10 gm. (ca. 70 m.mol) of 1-naphthol dissolved in 300 ml. of acetonitrile was added 100 ml of 10 N hydrochloric acid (ca. 1000 m.mol). The mixture was stirred at 80°. To it was added drop by drop 200 ml of 30% hydrogen peroxide (ca. 1800 m.mol) and stirred for 2 hr. The reaction mixture was filtered hot, cooled to room temp. and 400 ml of water was added. The crystals formed were filtered to give 10.2 gm (m.p. 116°) of 2-chloro-1,4-naphthoquinone. The filtrate was extracted with ether and the solvent was evaporated. The residue was crystallized from ethyl alcohol to give a further quantity of 1.2 gm (m.p. 116°) of 2-chloro-1,4-naphthoquinone (yield 85%).

Table I : Oxidation of Phenols and aromatic amines with hydrogen peroxide[a] and hydrochloric acid[b]

No.	Substrate[c]	Products[d]	Yield (%)
1	1-Naphthol	2-Chloro-1,4-naphthoquinone	85
2	2-tert.-Butyl-1-naphthol	2-tert.-Butyl-1,4-naphthoquinone	85
3	3-Methyl-1-naphthol	2-Chloro-3-methyl-1,4-naphthoquinone	82
4	6-Isopropyl-m-cresol (Thymol)	3-Chloro-5-isopropyl-2-methyl-p-benzoquinone	75
5	6-tert.-Butyl-o-cresol	2-Chloro-6-methyl-p-benzoquinone	50
6	6-tert.-Pentyl-o-cresol	2-Chloro-6-methyl-p-benzoquinone	55
7	2,6-Xylidine	2,6-Dimethyl-p-benzoquinone	30
		3-Chloro-2,6-dimethyl-p-benzoquinone	31
8	1-Naphthylamine	2-Chloro-1,4-naphthoquinone	65

a. The mole ratio of hydrogen peroxide for entries 1-7 was 26.6 and for 8 was 44.

b. The mole ratio of hydrochloric acid for 1-7 was 15 and for 8 was 25.

c. The reaction time for entries 1-6 was 2 hr. and for 7 & 8 was 3 hr.

d. Identity of the products was established on the basis i.r., n.m.r. and m.p.

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