

OXIDATION OF PHENOLS WITH HYDROGEN(HEXACYANOFERRATE(III))

L. Taimr and J. Pospíšil

Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences, Prague, Czechoslovakia

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In the present communication, we would like to point out the possibility of using hydrogen (hexacyanoferrate(III))⁺ for the oxidation of some phenols. The reaction proceeds in a homogeneous medium at room temperature within several minutes after a methanol solution of the phenolic derivative (1 mole) has been mixed with a methanol solution of the hydrogen(hexacyanoferrate(III)) (2.1 mole) and is completed by leaving the mixture to stand for 1/2-1 hour. The crude product is precipitated from the solution by diluting the reaction mixture with water. The examples are given in Table. The reaction also occurred in other alcohols, such as ethanol or ethyleneglycol.

Starting material	Product	M.p. °C	Yield, %
2,6-Di-tert.butylphenol	3,3',5,5'-Tetra-tert.butyl-1,1'-diphenoquinone ^{a)}	245-6	quantitative
2,6-Di-tert.butyl-4-methylphenol	2,6-Di-tert.butyl-4-methyl-4-methoxy-2,5-cyclohexadionone ^{b)}	93	28.0
	2,6-Di-tert.butyl-4-(methoxymethyl)phenol ^{b)}	99.5-101	2.4
2,6-Di-tert.butyl-4-methoxyphenol	2,6-Di-tert.butyl-1,4-benzoquinone	64-5	73.0

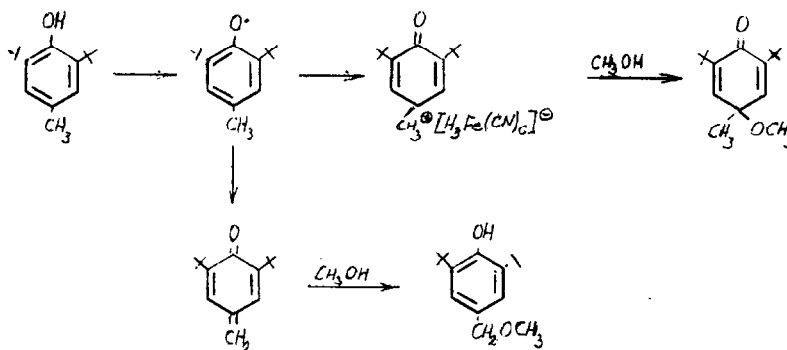
^{a)}The product precipitates immediately; ^{b)}The product was isolated chromatographically using a silicagel column.

Apparently, the oxidation is in all cases initiated by the elimination of hydrogen with the formation of an aryloxy group; the latter, in the case of 2,6-di-tert.butylphenol, dimerizes and after a further oxidation yields 3,3',5,5'-tetra-tert.butyl-1,1'-diphenoquinone, similarly to the oxidation with potassium ferricyanide in an alkaline medium (1). For 2,6-di-tert.butyl-4-methylphenoxyl, a disproportionation is assumed (2,3), yielding the initial phenol and 2,6-di-tert.butyl-

⁺The acid was precipitated from the solution of $K_3Fe(CN)_6$ by an excess of conc. HCl, filtered and dried over KOH. Before using, the crude acid was dissolved in MeOH, KCl was filtered off and the content of $H_3Fe(CN)_6$ in filtrate was determined by an iodometric titration.

1,4-quinonmethide, which in the benzene or tetrahydrofuran solution dimerizes (2), while in the presence of methanol it yields 2,6-di-tert.butyl-4-methoxymethylphenol (3). The latter compound is formed during oxidation with the hydrogen(hexacyanoferrate(III)) only as a by product. The main isolated product is 2,6-di-tert.butyl-4-methyl-4-methoxy-2,5-cyclohexadienone.

With respect to the mechanism considered by Coppinger (4) for the formation of the same compound during oxidation with bromine, a reaction scheme may be suggested:



The mechanism of oxidation of 2,6-di-tert.butyl-4-methoxyphenol is not quite clear; an analogy can be observed, however, with the formation of 2-tert.butyl-1,4-benzoquinone during oxidation of 2-tert.butyl-4-methoxyphenol (5) with vanadium pentoxide.

We have found that in alcoholic solutions, the hydrogen(hexacyanoferrate(III)) oxidizes phenols whose redox potentials (6) are lower than about 700 mV; (E° of the hydrogen(hexacyanoferrate(III)) was found (7) to be 692 mV). For instance, 4-methoxyphenol or an alkylated hydroquinone are very quickly oxidized, whereas already 2,4-di-tert.butylphenol (E° =760 mV) or 2-methyl-4,6-di-tert.butylphenol (E° = 730 mV) react only very unwillingly. Phenol or p-cresol do not react at all.

REFERENCES

1. C. D. Cook, E. S. English and B. J. Wilson, *J. Org. Chem.* **23**, 755 (1958).
2. R. Stebbins and F. Sicilio, *Tetrahedron*, **26**, 291 (1970).
3. C. M. Orlando, Jr., *J. Org. Chem.* **35**, 3714 (1970).
4. G. M. Coppinger, T. W. Campbell, *J. Am. Chem. Soc.* **75**, 734 (1953).
5. W. K. T. Gleim and A. Gaydasch, *US pat.* 2573136 (1951); *CA* **46**, 3566g (1952).
6. G. E. Penketh, *J. Anal. Chem.* **7**, 512 (1957).
7. P. Mohai, S. Papp and M. Sandor, *Veszpremi Vegyip. Egvet.* **8**, 107 (1964); *CA* **62**, 15747d (1965).