

Catalytic Oxidation of 2,6-Di-*t*-butyl-4-methylphenol by a Supported Iron Complex

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The catalytic oxidation of 2,6-di-*t*-butyl-4-methylphenol using a catalyst of $K_4[Fe(CN)_6]$ supported on acid-modified τ - Al_2O_3 is reported.

Many studies of the oxidation of substituted phenols, have been carried out.¹ Traditional stoichiometric oxidants or electro-oxidation methods have been used extensively,^{2,3} but catalytic oxidation by supported transition-metal complexes has not been reported previously.

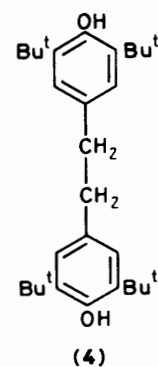
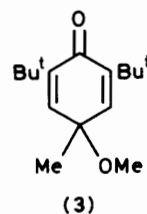
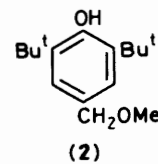
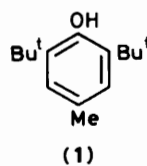
We report here the catalytic oxidation by a supported iron complex of 2,6-di-*t*-butyl-4-methylphenol (1) to 2,6-di-*t*-butyl-4-(methoxymethyl)-phenol (2) and 2,6-di-*t*-butyl-4-methyl-4-methoxy-cyclohexa-2,5-dienone (3) when the reaction is carried out in methanol suspension, or to 3,3',5,5'-tetra-*t*-butyl-4,4'-dihydroxybenzyl (4) when a chloroform suspension is used.

The catalyst was prepared by impregnation of an acid-modified τ - Al_2O_3 sample with an aqueous solution of $K_4[Fe(CN)_6]$ as reported elsewhere.^{4,5} During the adsorption step, a definite interaction of the $[Fe(CN)_6]^{4-}$ anionic species with the acid sites of the acid-modified surface of the support was established.^{5,6} Before the oxidation reaction iron was present only in the form of the $[Fe(CN)_6]^{4-}$ species anchored to the surface acid sites of the acid-modified τ -alumina, as determined by i.r. spectroscopy (broad band centred at 2065 cm^{-1}) and elemental microanalysis. After the reaction, a small quantity of $[Fe(CN)_6]^{3-}$ surface species was also present (a shoulder appears at 2120 cm^{-1}).

The catalytic oxidation was carried out at 303 K under irradiation from a Hg lamp at 550 nm with stirring and with O_2 bubbling. Only negligible oxidation of the phenol was observed in the absence of the catalyst, or in the presence of the catalyst but without irradiation or O_2 bubbling. After the reaction no iron could be detected in the solution.

The reaction mixture was separated by flash chromatography techniques, and the products were characterized by 1H n.m.r. and i.r. spectra, melting points, and elemental analysis. All compounds had satisfactory elemental analyses and data from their characterization by 1H n.m.r. and i.r. spectra and melting points were in agreement with those reported.⁷

In methanol suspension and after a reaction time of 12 h, 20% of the phenol (1) was oxidized to a mixture consisting of



66% of the ether (2) and 34% of the dienone (3). When the reaction time was extended to 24 h, 30% of the initial phenol (1) was oxidized and the product mixture was 83% of the ether (2) and 17% of the dienone (3). These results are in accord with those obtained by Brunow and Sumelius⁷ using $\text{H}_3[\text{Fe}(\text{CN})_6]$ as a stoichiometric oxidant, suggesting an isomerization of compound (3) to (2) for longer reaction times. In chloroform suspension, after a reaction time of 24 h, 20% of the initial phenol (1) was converted into the dimer (4). In both cases the conversions were chemically controlled.

These results show a parallel between the behaviour of $[\text{Fe}(\text{CN})_6]^{3-}$ when it is used as an oxidant in solution and that of the active catalytic species in the supported catalyst under our experimental conditions. On the other hand, a methanolic suspension of the catalyst was irradiated and bubbled with O_2 , leading to the partial oxidation of the initial species $[\text{Fe}(\text{CN})_6]^{4-}$ to $[\text{Fe}(\text{CN})_6]^{3-}$ on the surface (new sharp i.r. band at 2120 cm^{-1}). These facts suggest that the anchored $[\text{Fe}(\text{CN})_6]^{3-}$ is actually the active catalytic species, which is

formed from the initial $[\text{Fe}(\text{CN})_6]^{4-}$ by the 550 nm irradiation under oxygen.

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