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 stoicheiometric oxidants or electro-oxidation methods have been used extensively,[2,3] but catalytic oxidation by supported transition-metal complexes has not been reported previously.

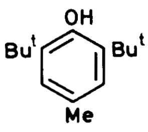
We report here the catalytic oxidation by a supported iron complex of 2,6-di-t-butyl-4-methylphenol (**1**) to 2,6-di-t-butyl-4-(methoxymethyl)-phenol (**2**) and 2,6-di-t-butyl-4-methyl-4-methoxy-cyclohexa-2,5-dienone (**3**) when the reaction is carried out in methanol suspension, or to 3,3′,5,5′-tetra-t-butyl-4,4′-dihydroxybenzyl (**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}).

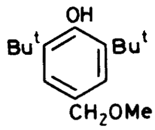
The catalytic oxidation was carried out at 303 K under irradiation from a Hg lamp at 550 nm with stirring and with O_2 bubbling. Only negligible oxidation of the phenol was observed in the absence of the catalyst, or in the presence of the catalyst but without irradiation or O_2 bubbling. After the reaction 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]

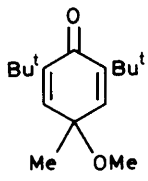
In methanol suspension and after a reaction time of 12 h, 20% of the phenol (**1**) was oxidized to a mixture consisting of



(1)



(2)



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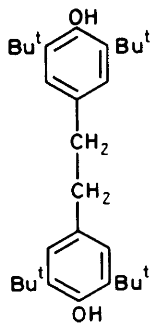

(4)

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 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 Sumelius[7] using $H_3[Fe(CN)_6]$ as a stoicheiometric 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 $[Fe(CN)_6]^{3-}$ 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 $[Fe(CN)_6]^{4-}$ to $[Fe(CN)_6]^{3-}$ on the surface (new sharp i.r. band at 2120 cm^{-1}). These facts suggest that the anchored $[Fe(CN)_6]^{3-}$ is actually the active catalytic species, which is formed from the initial $[Fe(CN)_6]^{4-}$ by the 550 nm irradiation under oxygen.

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