A Sterically Induced Deviation in Phenol Oxidation

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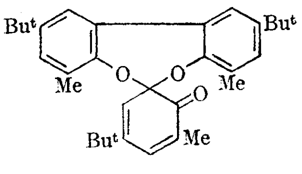
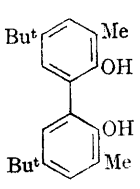
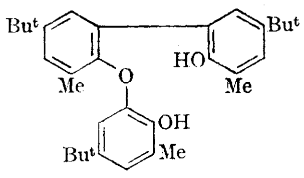
Oxidative coupling of *p*-cresol to Pummerer's ketone, clarified and applied by Barton, Deflorin, and Edwards to phloracetophenone, involves *ortho–para* C–C coupling.[1] The reaction has been shown to be general for *p*-alkylphenols with a free *ortho*-position.[2] In contrast we have recently found that monoalkyl-4-methoxyphenols typically couple to trimeric spiroketals under these conditions.[3] Here two mechanisms can operate, one involving initial *ortho–ortho* C–C coupling;[4] the other *ortho* C–O coupling as well.[5] In both series of phenols significant amounts of 2,2′-dihydroxybiphenyls, which are intermediate in spiroketal formation, are formed, and it is surprising that there is no interplay between these two series. The only example of spiroketal formation from a 4-alkylphenol is that of 4-t-butylguaiacol,[6] which is atypical in having a 2-methoxy-group which *per se* could account for spiroketal formation.



(I)



(II)



(III)

We have therefore oxidised 2-methyl-4-t-butylphenol, in which *ortho–para* coupling should be hindered by the t-alkyl group, and obtained the spiroketal (I) in 40% yield using silver oxide, though with alkaline ferricyanide only the dimer (II) can be isolated. This is the first example of such a trimer being obtained from a wholly alkylphenol rather than an alkoxy-phenol. That this effect is caused by steric hindrance to coupling in the *para*-position, and not by the choice of oxidant, is shown by our finding that oxidation of *p*-t-butylphenol by either reagent gives only polymer, and that 2,4-dimethylphenol, which has already been shown to give a Pummerer's ketone with ferricyanide,[2] also gives this with silver oxide. This conclusion is further supported by e.s.r. measurement of the hyperfine splitting constant of the *ortho*-hydrogens in the aryloxy-radicals derived from *p*-cresol,[7] *p*-t-butylphenol,[7] 2,4-dimethylphenol, and 2-methyl-4-t-butylphenol, which is constant at 6·0 œrsted.

The structure of the spiroketal (I) was established by its n.m.r. spectrum, by acid hydrolysis, which gave the dimer (II), by catalytic reduction to the phenoxybiphenyl (III), and by cleavage of the dimethyl ether of (III) with sodium in liquid ammonia, from which 3-methyl-5-t-butylguaiacol was isolated.

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