Radical Coupling in the Reaction of *o*-Halogenophenols with Base

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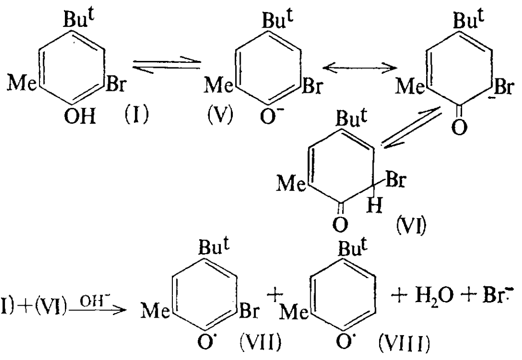
IT is many years since Hunter and his co-workers observed that the reaction between silver salts of 2,4,6-trihalogenophenols and alkyl iodides led to the transient appearance of a deep blue colour and resulted in the formation of polymeric "dihalophenylene oxides".[1] Though Hunter[2] and subsequent authors[3] have suggested mechanisms which involve aryloxy-radicals,[4] the absence of clearly defined products has hindered an understanding of the reaction. We now report some apparently related reactions of halogenophenols which do give discrete products.

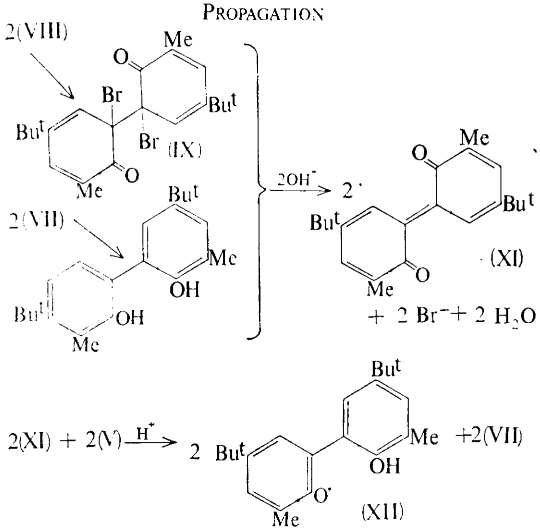
INITIATION



When solid potassium hydroxide was added to a solution of 2-bromo-6-methyl-4-t-butylphenol (I) in acetone or dimethylformamide, after a short induction period, a deep blue colour appeared near the alkali. On agitation the colour spread and eventually faded to yellow. The product, obtained in quantitative yield, was the spiroketal (II), while the halogen was recovered as potassium bromide. A similar reaction occurred with 2-bromo-4,6-di-t-butylphenol (III), giving the benzoxet (IV). Although products were obtained, the corresponding iodophenols reacted to a lesser extent.

That these products (II) and (IV) are precisely those obtained when 2-methyl-4-t-butylphenol[5] and 2,4-di-t-butylphenol[6] are oxidised by one-electron oxidants suggests a free-radical process. Signals, though ill-defined, were observed when bromophenols (I) and (III) were treated with base in the cavity of an e.s.r. spectrometer. The addition of traces of *o*-phenylenediamine, or of phenols which are more easily oxidised than the bromophenols, markedly inhibited the reaction, suggesting that a free-radical chain mechanism is involved. It was also noticed, when carrying out the reaction in a homogeneous system, that excess of alkali inhibited the reaction.

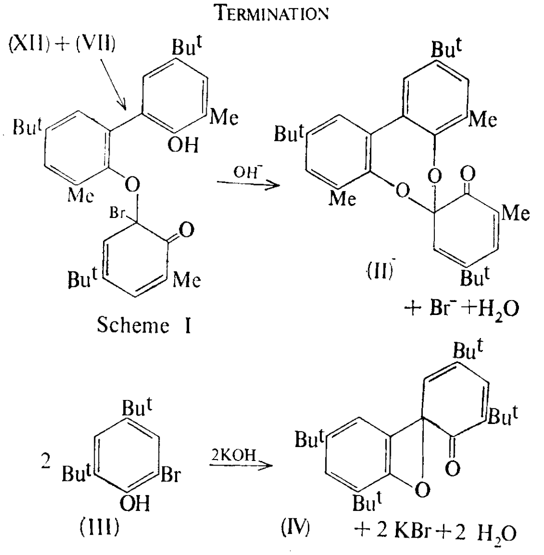
We therefore suggest the mechanism shown in the Scheme for the reaction of phenol (I). Though the reaction involves free radicals their origin was not immediately obvious, especially as the exclusion of light and oxygen had no inhibitory effect. An observation by Dimroth *et al.*[7] that the action of alkali on a mixture of chloro-2,4,6-triphenylphenol (formulated as the hypochlorite) and 2,4,6-triphenylphenol produces the radical 2,4,6-triphenylphenoxyl, suggested that the keto-tautomer of an *o*-halogenophenol might react similarly. Alkaline conditions are known to facilitate the formation of keto-tautomers of phenols.[8] We therefore suggest the initiation step of the Scheme, which is further supported by our finding that when a mixture of 4-bromo-2,4,6-tri-t-butylcyclohexa-2,5-dien-1-one and 2,4,6-tri-t-butylphenol in dimethylformamide is treated with aqueous potassium hydroxide 2,4,6-tri-t-butylphenoxyl is produced. This radical cannot be formed by treating the bromo-compound alone with base.



$$2(\mathrm{VII}) \longrightarrow (\mathrm{IX}) \longrightarrow (\mathrm{XI}) + \mathrm{Br}_2$$

$$\mathrm{Br}_2 + 2(\mathrm{V}) \longrightarrow 2\,\mathrm{Br}^- + 2(\mathrm{VII})$$

In the propagation steps the most obvious chain-transfer agent is bromine radical, which can be derived from compound (IX). The formation and debromination of the latter finds analogy in bis-(1-bromo-3,5-di-t-butylcyclohexa-2,5-diene-4-one) which loses bromine spontaneously.[9] All known quinones of type (XI) are blue,[10] and the transient blue colour of the reaction mixture is attributed to the presence of compound (XI). The suggested reduction of the latter to (XII) by an electron exchange with the anion (V), and protonation, is paralleled by the similar reduction of a dipheno-4,4′-quinone recently described by Bacon and Stewart.[11] Evidence for the oxidation of phenol anions to radicals by halogens will be presented in detail later. Ample analogy exists for the termination step. In modified form this mechanism is clearly applicable to the formation of the benzoxet (IV) from phenol (III).



Scheme I

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