Oxidative Coupling of Phenols by Diphenoquinones

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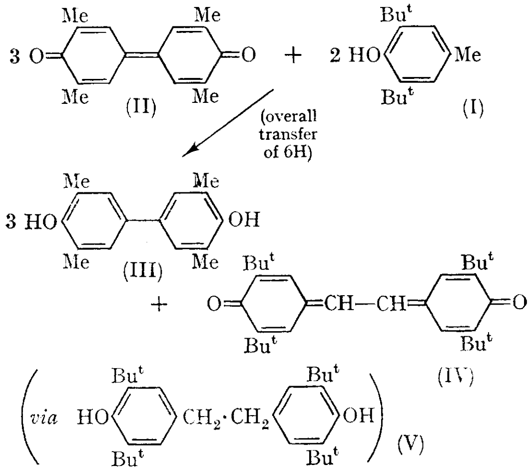
WHILE studying copper-catalysed hydrogen-transfer reactions between various organic species,[1] we observed that oxidation–reduction could readily occur in solution between a phenol and a diphenoquinone, without catalysis by copper. We record an example of this non-catalysed type of hydrogen transfer because of its mechanistic interest and also in view of related examples, involving different conditions, which have been reported from another laboratory.[2] There the recommended procedure was to use an amine to promote the oxidation-reduction.

Reaction between 2,6-di-t-butyl-4-methylphenol (I) and 3,3′,5,5′-tetramethyldiphenoquinone (II), employed in equimolar proportions, was carried out under nitrogen in a refluxing solvent. Chromatography of the product on alumina furnished 4,4′-dihydroxy-3,3′,5,5′-tetramethylbiphenyl (III) and 3,3′,5,5′-tetra-t-butylstilbenequinone (IV), both in yields of up to about 90%; small amounts of the intermediate diphenylethane derivative (V) were isolated in some cases:



Substantial conversions occurred in chloroform (at 61°), whilst reaction for 2 hr. in benzene (at 80°) furnished ~80% of (III) and (IV); yields were still better in *o*-xylene (at 144°), but were somewhat inferior in 2,4,6-collidine, a basic solvent (at 170°). No significant improvement resulted if cuprous oxide was present. At the higher reaction temperatures the interpretation of data may be complicated by an independently occurring disproportionation reaction:

(II) → (III) +
resinous dehydrogenation products of (II).

We have encountered this type of reaction on other occasions and an example has long been known in the case of *p*-benzoquinone.[3]

The dehydrogenation of certain types of organic compounds by quinones[4] is considered to proceed by a heterolytic mechanism,[4,5] whereby the quinone gains, and the donor loses, a hydride ion and a proton. A diphenoquinone (usually the 2,2′,6,6′-tetrachloro-derivative) has occasionally been used in place of a quinone, though, until the recent reference[2] to phenols or diphenylmethane as substrates, the few examples on record[6] were restricted to dehydrogenation of partially unsaturated cyclic compounds or bibenzyl.

By contrast with the ionic mechanism proposed for quinone reduction, a homolytic mechanism is commonly suggested for the oxidative coupling of a phenol;[7] single-electron transfer and proton loss from the phenol produce the intermediate phenoxy-radicals. The probable first step in the interaction of (I) and (II) is formation of a molecular complex.[8] Mechanistic alternatives for the subsequent hydrogen-transfer process are (*a*) that the oxidative coupling,[9] (I) → (V) involves ionic intermediates (as in the accompanying reduction) or (*b*) that the quinone reduction, (II) → (III), involves radical intermediates (as in the accompanying oxidation); either view is contrary to that usually held for the type of reaction concerned.

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[9] The coupling of this phenol occurs at its methyl group, but a homolytic mechanism has been suggested for the reaction, as in the commoner cases of phenols undergoing coupling at nuclear positions (W. A. Waters, "Mechanisms of Oxidation of Organic Compounds", Methuen, London, 1964, p. 144).