# Coupling of Phenols *via* an Anodically Generated Phenoxonium Ion

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Summary Anodic oxidation of 2,6-di-t-butyl-*p*-cresol (I) in the presence of phenol, anisole, or 2,6-di-t-butylphenol gives the unsymmetrically coupled cyclohexa-2,5-dienones (VIII), (IX), and (X) *via* a mechanism involving the phenoxonium ion (III).

THE coupling of a phenoxonium ion with a phenol or a phenol ether has been suggested[1] as a possible mechanism for the oxidative coupling of phenols under special circumstances, but no unambiguous cases of such couplings have been reported.[2]

SCHEME 1
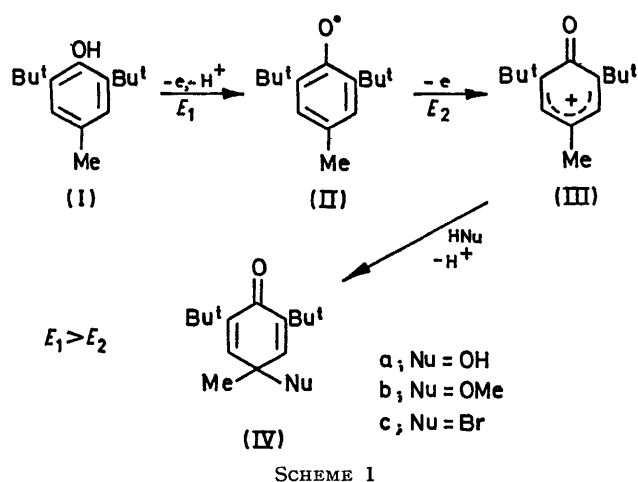
Recently[3] we have shown that the primary step in the anodic oxidation of 2,6-di-t-butyl-p-cresol (I) in neutral or slightly basic solution is the formation of the phenoxonium ion (III) which reacts with simple nucleophiles such as H_2O or MeOH with selective formation of 4-substituted cyclohexa-2,5-dienones (IVa and b). The same selectivity was observed when these two dienones (IVa and b) were prepared from the bromodienone (IVc) by silver-induced solvolysis.[3] In an electrochemical study of 2,4,6-tri-aryl-phenols Dimroth et al.[4] isolated the hexachloroanti-monate salts of the corresponding phenoxonium ions and showed that these salts react with H_2O or MeOH with selective formation of 4-substituted cyclohexa-2,5-dienones.

These findings indicated that the feasibility of coupling phenols via phenoxonium ions could be tested by oxidizing (I) at a controlled potential in the presence of a suitable phenol or phenol ether with a higher oxidation potential. The halfwave potentials of a few such compounds are give in Table 1. The results from oxidation of (I) in the presence of these compounds are shown in Table 2. Fair yields of

TABLE 1

| Compound					Halfway potential (in V)[a]
(I)	..	..	..	..	1·21
Phenol (V)	..	..	..	..	1·34
Anisole (VI)	..	..	..	..	1·76
2,6-Di-t-butylphenol (VII)	..	..		1·41

[a] Halfwave potentials were measured in 0·1 mM solutions in acetonitrile containing $LiClO_4$ (0·1 M) as supporting electrolyte vs. the standard calomel electrode (SCE).

coupled products (VIII)—(X), identified by the data in Table 3, are obtained. As the compounds (V)—(VII) are not oxidized appreciably at the potential applied we can exclude mechanisms involving oxidized forms in the formation of coupled products. Furthermore the yield of the coupled product is strongly dependent on the amount of water present in the electrolysis mixture. If a two-fold molar excess of water over (I) is added in experiments similar to those in Table 2 the formation of the coupled

(VIII); R = H
(IX); R = Me
(X)
(XI)
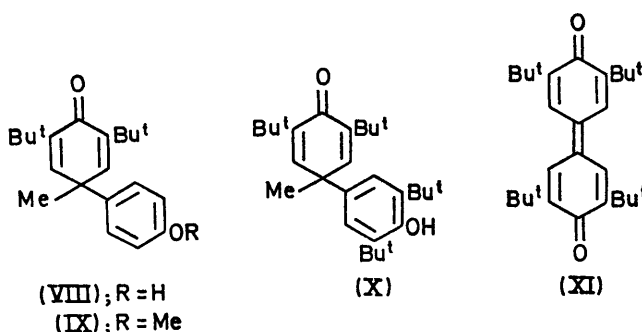
product is completely suppressed (addition of methanol has the same effect). If the coupled product was formed by attack of the radical (II) on (V), (VI), or (VII) followed by oxidation the yield of the coupled product should be independent of the concentration of water since the radical (II) does not react with water. In view of this and our previous results[3] the only reasonable mechanism for the formation of the coupled products (VIII)—(X) involves primary formation of the phenoxonium ion (III) followed by coupling with the phenol or phenol ether in a normal electrophilic aromatic substitution. It is interesting that in all three experiments we have been able to detect only one of the various possible coupling products (e.g. no ortho-substitution).

Phenoxonium ions are apparently generated when phenols are oxidized in neutral or acidic solution with one-electron oxidants. E.g. oxidation of 2,6-dimethylphenol (XII) with the hexachloroiridate(IV) anion[5] at pH 4 or with ferric chloride[6] in neutral solution gives a 27 or 14% yield of 2,6-dimethyl-p-benzoquinone (XVI) which is probably formed as shown in Scheme 2.† The radical (XIII) might

SCHEME 2
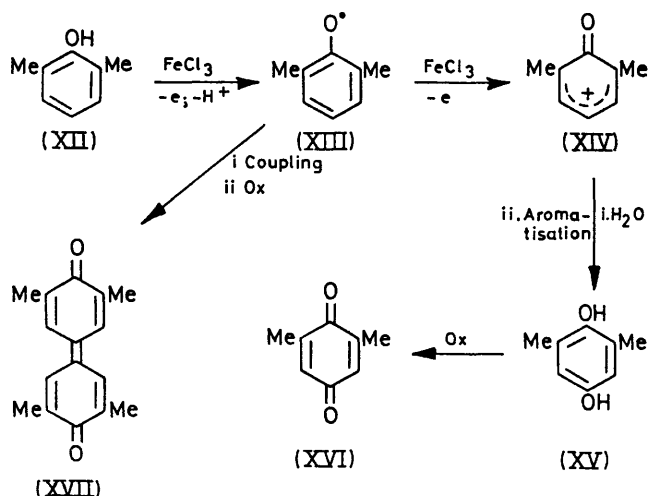
undergo further oxidation‡ or dimerisation. The latter is faster since dimeric (and polymeric) products predominate.

† The reactive intermediates are drawn as free species but they could very well be complex bound to Fe[III] or Fe[II].

‡ The radical is more easily oxidized than the phenol.

TABLE 2

Products and yields from anodic oxidation at constant potential of 2,6-di-t-butyl-p-cresol (I) in the presence of phenol (V), anisole (VI), or 2,6-di-t-butylphenol (VII)[a].

Phenols			Potential (in V)[e]	Current consumed [F/mol of (I)]	Chemical yield (%)[f]
(I) and (V)[b]	..	..	1·27	4·0	(I) (2); (IVa) (50);(VIII) (20)[g]
(I) and (VI)[c]	..	..	1·27	4·0	(I) (5); (IVa) (11); (IX) (81)[h]
(I) and (VII)[b]	..	..	1·27	4·0	(I) (2); (IVa) (58); (X) (40)[i]
(VII) alone[d]	..	..	1·56	3·6	(VII) (15); (XI)(85)

[a] In all experiments acetonitrile was the solvent with $Bu^n_4NBF_4$ (0·1 M) as supporting electrolyte, platinum as anode, and carbon as cathode. No diaphragm was used. Although precautions were taken to keep moisture out of the cell the electrolysis solution always contained some water which explains the formation of (IVa). [b] 40 mM in each phenol. [c] 40 mM in (I) and 0·2 M in (VI). [d] 40 mM in (VII). [e] *Vs.* SCE. [f] Based on (I). [g] 70% of (V) was recovered unchanged. [h] No products derived from oxidation of (VI) were detected. [i] 40% of (VII) was converted into (X), 8% into (XI), and 51% of (VII) was recovered unchanged.

By anodic oxidation in 1N-sulphuric acid [i](PbO$_2$ anode) or in acetonitrile–water (1:1) (platinum anode) (XII) can be converted quantitatively into (XVI).[7] Even this oxidation is thought to proceed *via* the mechanism in Scheme 2. In this case however the radical (XIII) when formed will be adsorbed on the anode and since it is more easily oxidized than the phenol (XII) it will be immediately oxidized further to the phenoxonium ion (XIV) (mass-transfer control

proceeds *via* a six-membered phenol–oxidant complex without intermediate formation of a phenoxonium ion.

The mechanism suggested here for the anodic coupling of phenols is similar to the ionic mechanism suggested by Hamilton[9] for the enzymatic coupling of phenols in living organisms. The anode in the present case might thus be considered as a simple model for the specific metalloenzymes[9] involved although their existence is yet to be proved.

TABLE 3

Physical and spectroscopic data for the coupling products (VIII)—(X)

Compound	M.p. (°C)	N.m.r. (δ p.p.m.)[b]	I.r. (cm^{-1})[c]	Mass spectrum[d]
(VIII)	187—188	1·25 (s, 18H); 1·63 (s, 3H); 6·69 (s, 2H); 7·00 (q, J 9·5 Hz, 4H)	3430, 1655, 1633, 1618, 1598	312 (M^+) 297, 256*
(IX)	107—108	1·24 (s, 18H); 1·60 (s, 3H); 3·72 (s, 3H); 6·50 (s, 2H); 6·99 (q, J 9·5 Hz, 4H)	1665, 1648, 1515	326 (M^+), 311, 295, 270*, 255
(X)[a]	157—158	1·25 (s, 18H); 1·43 (s, 18H); 1·59 (s, 3H); 5·05 (s, 1H); 6·50 (s, 2H); 7·00 (s, 2H)	3640, 1660, 1640	424 (M^+), 409, 368*

[a] This compound has been obtained previously in low yield (5·3% and 1·5%) by nickel peroxide oxidation of (I) [J. Sugita, *Nippon Kagaku Zasshi*, 1966, 87, 1082 (*Chem. Abs.*, 1967, 66, 94 777w)] and by cuprous chloride–amine catalysed reaction of (I) with oxygen (C. M. Orlando, *J. Org. Chem.*, 1968, 33, 2516). In contrast no detectable amounts of (X) are formed by anodic oxidation of (I) at controlled potential (1·27 V). [b] The n.m.r. spectra of (IX) and (X) were recorded in carbon tetrachloride and that of (VIII) in hexa-deuterioacetone with Me$_4$Si as internal standard. [c] For KBr discs. [d] Base peak is marked with an asterisk.

of the oxidation). Similarly two-electron oxidants such as NaIO$_4$ would be expected to oxidize phenols *via* phenoxonium ions. In fact quinones derived from hydroxylated products are formed by NaIO$_4$ oxidation of various phenols[8] but the isomer distribution found[8] (high yields of *ortho*-hydroxylated products) indicates that this oxidation

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