Anodic Cleavage of Carbon–Oxygen Bonds in Diaryl Ethers

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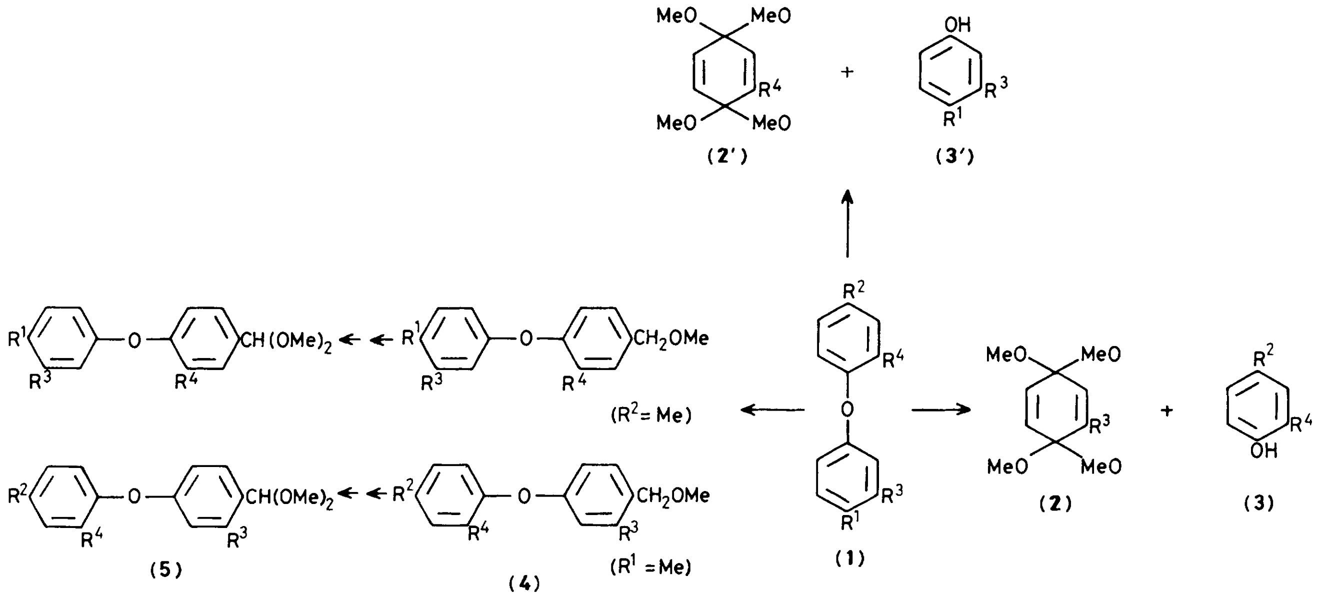
Diaryl ethers (**1**), which are model compounds for important linkages in lignins, are cleaved efficiently and conveniently by constant current anodic oxidation in methanol; the bis-acetals (**2**) are the main products (in 50—80% yield).

The diaryl ether linkage forms the cross-link in many lignins.[1] There is considerable current interest in methods for depolymerization of lignins for the production of phenols of lower molecular weight. There are few useful chemical methods for such cleavage.[2] By analogy with classical oxidative methods for lignin degradation[3] anodic cleavage might be expected to be effective; however for alkyl aryl ethers it has been found that only alkyl–oxygen fission accompanies electrochemical oxidation.[4] By contrast the electrochemical behaviour of diaryl ethers has not been examined. We report here on an



Scheme 1

Table 1. Electrochemical oxidation potentials.[a]

Compound		$E_p^a(1)$/V	$E_p^a(2)$/V
(**1a**)	$R^1 = R^2 = R^3 = R^4 = H$	2.25	2.84
(**1b**)	$R^1 = OMe; R^2 = R^3 = R^4 = H$	1.92	2.36
(**1c**)	$R^1 = R^2 = OMe; R^3 = R^4 = H$	2.04	2.31
(**1d**)	$R^1 = OMe; R^2 = Me; R^3 = R^4 = H$	1.91	2.19
(**1e**)	$R^1 = Me; R^2 = R^3 = R^4 = H$	2.18	2.38
(**1f**)	$R^1 = R^2 = Me; R^3 = R^4 = H$	2.15	2.39
(**1g**)[b]	$R^1 = R^3 = R^4 = OMe; R^2 = H$	1.59	1.61
(**1h**)[b]	$R^1 = R^2 = R^3 = OMe; R^4 = H$	1.58	1.72
(**1i**)[b]	$R^1 = R^4 = OMe; R^2 = Me; R^3 = H$	1.90	2.22

[a] Pt bead anode; reference electrode Ag/AgI; MeCN/0.1 M NaClO$_4$; scan rate 0.2 V s^{-1}. [b] These new compounds gave satisfactory microanalytical and spectral data in agreement with the assigned structures.

Table 2. Constant current oxidation of diaryl ethers (**1**).[a]

Diaryl ethers (**1**)	Products (% yield)[b]
(**1b**)	(**2**) (58); (**3**)[c]
(**1c**)	(**2**) (71); (**3**)[c]
(**1d**)	(**2**) (53); (**3**)[c]
(**1e**)	(**4**) (17); (**5**) (37)[d]
(**1f**)	(**4**) (28); (**5**) (36)[d]
(**1g**)	(**2**) (78); (**3**)[c]
(**1h**)	(**2**) (59); (**3**)[c]
(**1i**)	(**2**) (60); (**3**)[c]

[a] Electrolysis conditions: MeOH–0.5 M MeONa; Pt foil anode and cathode; undivided cell; current density 0.025 A cm^{-2}; 4—5 F mol^{-1}. [b] Isolated by column chromatography after aqueous work-up. [c] Products detected in aqueous phase after acidifying. [d] 10 F mol^{-1}.

examination of the anodic reactions of the diaryl ethers (**1**) which includes compounds substituted as in lignins.

The most important result is that reactions are dominated by carbon–oxygen cleavage, a finding likely to be significant for methods of lignin depolymerization. The possible routes for oxidative cleavage in methanol are shown in Scheme 1.

Cyclic voltammetry (Table 1) shows that the oxidation potentials of the diaryl ethers are affected by ring substitution in a predictable fashion. In general methoxy substitution lowers the oxidation potentials more than methyl substitution.

Preparative scale electrolysis, in an undivided cell and at constant current, was clean and efficient. Product analysis (Table 2) reveals that the bis-acetals (**2**) are the main products and the major factor governing the direction of cleavage is a requirement for 4-methoxy substitution. Where both R^1 and R^2 are methoxy the bis-acetal is formed from the more easily oxidized ring. The parent compound (**1a**) is not cleaved and it is also the least easily oxidized compound; it is probable that in this case the necessary oxidation potential is not reached under constant current conditions in methanol. Methyl substitution alone is sufficient to activate the compounds towards oxidation but in these cases (**1e,f**) the products are those of side chain substitution, (**4**) and (**5**).

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