Oxidative Coupling of Some 2,6-Disubstituted Phenols

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The oxidative coupling of several 2,6-disubstituted phenols by means of oxygen–cuprous chloride–pyridine, manganeese dioxide, silver oxide and lead dioxide to yield poly(phenylene ethers) and/or 4,4'-diphenoquinones is described. Although there are exceptions, lead dioxide is the most generally useful oxidizing agent for polymer formation; silver oxide is particularly useful for preparing 4,4'-diphenoquinones.

THE nature of the products derived from the oxidative polymerization[1] of 2,6-disubstituted phenols with one-electron oxidizing agents depends to a large extent on the size of the substituents: with small groups, e.g. methyl, poly(phenylene ethers) predominate, but with bulky groups, e.g. *t*-butyl, 4,4'-diphenoquinones are formed almost exclusively. Both types of product result from radical–radical coupling reactions, but the polymers arise from quinol ethers, formed by C—O coupling, *via* redistribution[2], whereas the quinones are formed by C—C coupling followed by oxidative dehydrogenation. Although the mechanisms of these reactions have received fairly extensive study[3], the relative efficiencies of various oxidizing agents have been less widely examined.

The present paper describes the oxidation of several 2,6-disubstituted phenols with the oxygen–cuprous chloride–pyridine system, and with manganese dioxide, silver oxide and lead dioxide. Results for the oxidation of some phenols carrying additional substituents in the 3- and/or 5-positions are also given.

EXPERIMENTAL

Phenols were commercial samples, and were purified by crystallization and/or distillation followed, for solids, by zone melting except for 2,6-dimethylphenol which for some experiments (see *Table 2*) was only distilled. Solvents were distilled, pyridine from solid potassium hydroxide. Cuprous chloride was purified by dissolving it in concentrated hydrochloric acid, precipitating with water, and washing the precipitate with ethanol and ether; it was then dried in a desiccator.

Polymerization procedures

  Polymerizations were carried out at 20°C.

  (*a*) The phenol (0·082 mole) was added to a solution of cuprous chloride (0·022g) in a mixture of pyridine (5 cm³) and nitrobenzene (17 cm³), and oxygen was bubbled through the vigorously stirred solution for one hour. Methanol was then added to precipitate the polymer, and the diphenoquinone was subsequently isolated from the mother liquor by removal of the solvent under reduced pressure.

  (*b*) For *Table 1*. Manganese dioxide[4] (2·2g) was added to a solution of the phenol (0·082 mole) in toluene (10 cm³), the mixture was stirred for

17 h and the manganese dioxide was then removed by filtration and washed with benzene (30 cm³). The filtrate and washings were combined, and the polymer was precipitated by addition of methanol. Removal of the solvent from the mother liquor gave the diphenoquinone.

(c) A mixture of the phenol (0·082 mole), silver oxide[5] (3·3g) and benzene (10 cm³) was stirred for 17 h, and then worked up as described under (b).

(d) As procedure (b) but using lead dioxide (5·5g, B.D.H.).

Products

The polymers were purified where possible by dissolution in benzene or toluene followed by precipitation with methanol. The polymer from 2,3, 6-trimethylphenol was almost insoluble in all the common solvents except 1-chloronaphthalene from which it could not be precipitated by addition of methanol. The polymers were characterized by their infra-red and proton magnetic resonance spectra, which were consistent with the assigned structures.

The diphenoquinones were purified by crystallization from light petroleum, and where possible were compared with authentic samples. 3,3′,5,5′-Tetra-*t*-butyl-4,4′-diphenoquinone had m.pt 246°–247°C (lit.[6] 246°–247°); 3,3′,5,5′-tetraisopropyl-4,4′-diphenoquinone had m.pt 198°–199°C (lit.[7] 196°–197°C); 3,3′,5,5′-tetramethoxy-4,4′-diphenoquinone had m.pt 272°–273°C (lit.[4] > 300°; cf. ref. 8). 2,2′,3,3′,5,5′,6,6′-Octafluoro-4,4′-diphenoquinone was obtained as brown crystals, m.pt 102°–103°C (Found: C, 44·1; F, 46·4. $C_{12}F_8O_2$ requires C, 43·8; F, 46·3 per cent); it had $\nu_{max.}$ (in CHCl₃) 1 638 cm⁻¹, and $\lambda_{max.}$ (in EtOH) 260 mμ (ϵ 51 000) with $\lambda_{infl.}$ 300 mμ (ϵ 10 000).

RESULTS AND DISCUSSION

The oxidation results are summarized in *Table 1*. An early step in the oxidation is the removal of a hydrogen atom from the hydroxyl group of the phenol to give a phenoxyl radical from which the products are derived:
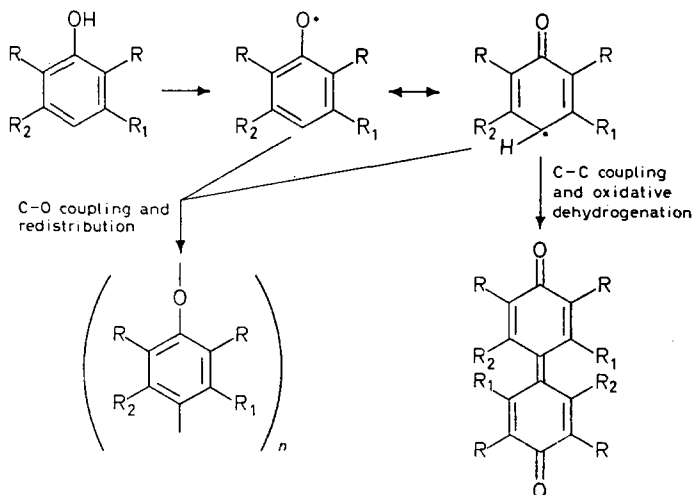
Table 1. Isolated yields of poly(phenylene ethers) (P) and 4,4'-diphenoquinones (Q) obtained from 2,6-disubstituted phenols and various oxidizing agents

(See formula, p 702)			Oxidant: O_2–CuCl–PyH			MnO_2			Ag_2O			PbO_2		
			Yield (%)		$\overline{M}_v$ of P	Yield (%)		$\overline{M}_v$ of P	Yield (%)		$\overline{M}_v$ of P	Yield (%)		$\overline{M}_v$ of P
R	R_1	R_2	Q	P	(a)	Q	P	(a)	Q	P	(a)	Q	P	(a)
Me	H	H	—	80	10^5(b)	—	85	10^5	—	50	3×10^4(c)	—	85	10^5
Me	Me	H	—	90	4×10^4	—	15	4×10^4	—	14	4×10^4	—	13	3×10^4
Me	Me	Me	—	—		—	22	3×10^3	—	15	3×10^3	—	25	3×10^3
Pr^i	H	H	40	—		55	—		55	7		—	75	
Bu^s	H	H	49	—		63	—		61	8	$1\cdot5\times10^3$	81	1	
Bu^t	H	H	97(c)	—		71	—		80(b)	—		92	—	
MeO	H	H	52	—		—	—		—	—		—	37	
Cl	H	H	—	—		—	14	10^4	—	60	2×10^4	—	65	
F	F	F	—	—		—	—		95	—		41	0·1	3×10^3

(a) Calculated from the relationship $[\eta]=2\cdot60\times10^{-4}$ $(\overline{M}_v)^{0\cdot64}$ derived for poly(2,6-dimethylphenylene ether); the data for the other polymers are therefore approximate.
(b) Ref. 1. (c) Ref. 10.

This oxidation will be governed at least to some extent by the oxidation potential (E_0) of the catalyst. Thus on this basis the order of effectiveness for the heterogeneous systems should be PbO_2 ($E_0 = 1.46$ V; ref. 11a) > Ag_2O ($E_0 = 0.80$ V; ref. 11b) > MnO_2 ($E_0 = 0.2$ V; ref. 11c). This pattern can be seen for some of the phenols listed in *Table 1*, but it is by no means generally clear either for polymer formation or quinone formation, and steric effects due to the substituents on the phenolic nucleus may play an important part. Apparently small changes in the steric effect in the immediate vicinity of the hydroxyl group may exert a major influence on product formation. Thus although both 2,6-di-isopropyl- and 2,6-di-sec-butyl-phenol give fair yields of quinones with oxygen–cuprous chloride–pyridine, manganese dioxide and silver oxide, a striking difference is apparent for lead dioxide: the di-isopropylphenol yields 75 per cent of polymer whereas the di-sec-butylphenol gives 81 per cent of quinone.

The low yields of the polymers, and their comparatively low molecular weights, formed from 2,6-di-isopropyl-, 2,6-di-sec-butyl- and 2,3,5,6-tetramethyl-phenol are probably due to steric interference with the C—O coupling reaction. 2,6-Di-t-butylphenol behaves as expected with all the oxidizing agents, giving the diphenoquinone since C—O coupling is sterically prevented.

The low yields of polymer from 2,3,6-trimethylphenol may be due to the comparatively low solubility of the polymer, and to adsorption of at least a part of it on to the catalyst; treatment of the insoluble residue from a manganese dioxide polymerization with concentrated hydrochloric acid to dissolve the inorganic material left a high yield of polymer which, however, contained some chlorine.

2,6-Dimethoxyphenol is unusual in that it yields a polymer only with lead dioxide, and the diphenoquinone only with the oxygen–cuprous chloride–pyridine system.

A series of experiments was conducted in order to determine the optimum conditions for the polymerization of 2,6-dimethylphenol. The results are summarized in *Table 2*.

Table 2. Polymerization of 2,6-dimethylphenol (1g) with manganese dioxide (2·2g) in toluene (10 cm³) at 20°, with continuous stirring

No.	MnO_2	Reaction time, h	Additive	Atmosphere	$[\eta]$ (f)	$\overline{M}_v$ (f)
1	(a)	36	—	N_2	0·1	8 900
2	(b)	36	—	N_2	0·3	22 500
3	(b)	24	(e)	N_2	0·36	30 000
4	(c)	16	(e)	N_2	0·61	95 000
5	(c)	16	(e)	N_2	0·63	110 000
6	(c)	16	(e)	Air	0·68	150 000
7	(c)	16	(e)	Air	0·70	152 000 (g)
8	(d)	16	(e)	Air	0·59	90 000

Runs 1–4: phenol purified by distillation. Runs 5–8: phenol purified by distillation followed by zone melting. (a) Ref. 12. (b) Ref. 13. (c) Ref. 14. (d) Ref. 13: product ground to pass 200 mesh sieve. (e) Cetyltrimethylammonium bromide (0·03g) present. (f) $[\eta]$ Determined at 25° for solutions in benzene; $\overline{M}_v$ calculated from the relationship' $[\eta] = 2.60 \times 10^{-4}$ $(\overline{M}_v)^{0.64}$. (g) Yield 80 per cent. Other runs gave somewhat lower yields.

Careful purification of the phenol, and the presence of both a quaternary ammonium compound and air favour the formation of high molecular weight polymer. Purification probably removes chain-terminating agents. The function of the quaternary ammonium additive[15] is not clear, but in the presence of air it may assist in the coupling reaction; it is known[16] that exposure of benzene solutions of the polymer to air in the presence of aqueous potassium hydroxide causes an increase in molecular weight, a phenomenon confirmed during the course of the present work.

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