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THE OXIDATION OF PHENOLS WITH CHROMYL CHLORIDE—II

2,5-, 2,6- and 3,5- DIALKYL PHENOLS

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Abstract—It has been shown that the oxidation of alkyl phenols with chromyl chloride gives *p*-benzoquinone, in yields which depend on the mole ratio of reactants, the position of the substituent on the ring, and, the nature of the alkyl substituent.

DISCUSSION

THE reactions of phenols and phenoxy radicals have been described in detail in reviews.[1-3]

While some non-radical mechanisms have been described[4,5] for phenol oxidation it would appear that in most reactions the first stage is the formation of a phenoxy free radical.

$$\mathrm{ArOH + Ox \rightarrow ArO\cdot + OxH}$$

Further stages in the reaction are determined by the stability of the radical and in particular by the rate at which it reacts either with another radical to give a coupled product or with the oxidant to give a quinone.

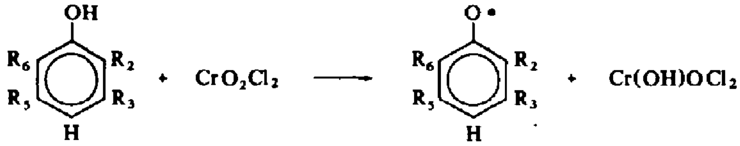
The oxidation of mono- and di-alkyl substituted monohydric phenols can give both quinones and products resulting from coupling. Phenols which have the largest groups in the *ortho* positions give the most stable radicals:[6] in the presence of strong oxidizing agents it is they which give the highest yields of quinones. This latter point is demonstrated by the results obtained by Teuber[7] who used Fremy's salt as oxidant. He found for the methyl substituted phenols that the yield of quinone increased along the series *m*-cresol, 3,5-dimethylphenol, *o*-cresol, 2,5-dimethylphenol, 2,6-dimethylphenol. Similarly Forrester and Thomson[8] using organic nitroxides obtained high yields of quinone from 2,6-dimethylphenol but no quinone at all from *o*-cresol. The reactions described in this paper and in an earlier paper[9] indicate that the yield of quinone, obtained by the chromyl chloride oxidation of phenols, increases with the degree of substitution in the *ortho* position.

The effect of using different oxidants on the same phenol can be quite marked. For example, the oxidation of the 2,6-dialkylphenols with strong oxidizing agents can give either the *p*-benzoquinone or the diphenoquinone. The nitroxides[7,8] and peroxyacetic acid[10] give high yields of quinone but no diphenoquinone while, hydrogen peroxide in acidified ferrous sulphate,[11] alkaline ferricyanide,[12] acyl peroxide,[13] persulphate in the presence of silver ions,[14] and lead dioxide[15] give high yields of diphenoquinone with little or no quinone. Cavill *et al.*[16] using lead tetraacetate and Horswill and Ingold[17] using peroxy radicals, have obtained both the quinone and the diphenoquinone (in the former case under different mole ratio conditions, in the latter case under the same conditions).

The oxidation of 3,5- and 2,5-dialkylphenols has not attracted much attention. Good yields of quinone have been obtained using Fremy's[7] salt and peroxyacetic[10] acid, but the persulphate[14] oxidation of the 3,5-dimethylphenol gives resin only.

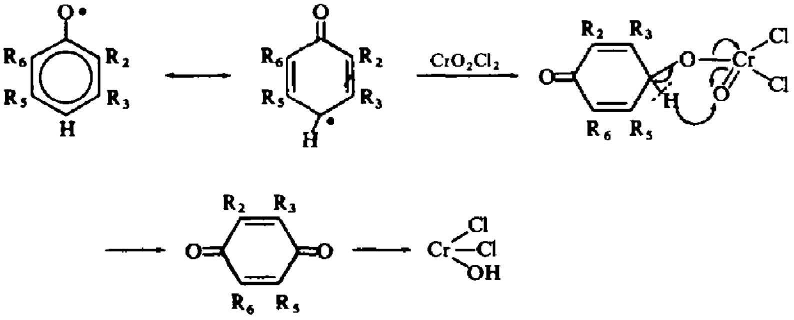
Our results show that, like the chlorophenols, described in an earlier paper[9] the dialkyl phenols react with chromyl chloride to give brown amorphous solids which on hydrolysis yield the oxidized forms of the phenols. We have shown that the yield of quinone varies with the nature and position of alkyl substituents and with the mole ratio of reactants. An examination of the other products formed in the reactions shows the formation of diphenoquinone from the 2,6-dialkyl phenols and polymeric compounds from all the phenols. Although pure compounds have not been isolated, the mass spectra of some of the tars indicated the presence of dimeric and trimeric polyphenols. The formation of these polymeric products and the diphenoquinones points to a radical mechanism rather than the ionic process described previously.[9]

The first stage of the oxidation reaction is probably

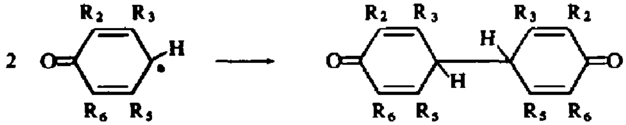


That the reduction of chromyl chloride to a Cr (V) species is possible is indicated by work of Krauss *et al.*[18]

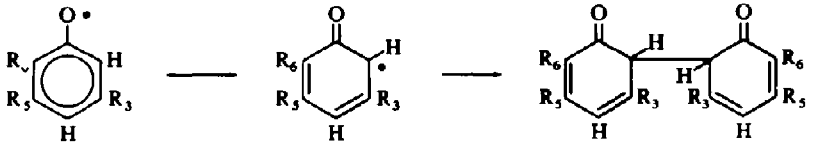
The second stage that leads to the formation of the quinone can be written (cf. the reaction with Fremy's salt[19])



An alternative second stage reaction is the coupling of the radicals via the C atoms



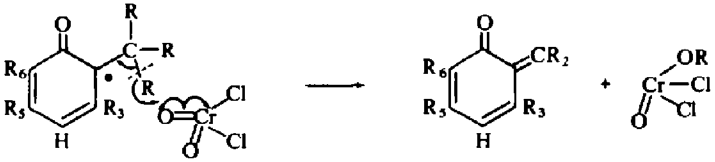
or if R_2 and/or R_6 are hydrogens



Another possibility is carbon–oxygen coupling to give polyphenylene ethers.[20–22] Quinone formation is expected to be favoured in cases in which the radical does not couple rapidly, decompose or react through its side chain. That the yield increases with the stability of the radical is exemplified by the results obtained from the reactions of *o*-cresol, 2,6-dimethylphenol and 2,6-di-t-butyl phenol. Again comparison of the results obtained from the 3,5-, 2,5- and 2,6-dimethylphenols shows the effect of *ortho* substituents on the yield of quinone.

The dependence of the yield of quinone on the mole ratio of oxidant to phenol can be explained in terms of radical stability and side chain attack. For the unstable radicals the greater the excess of oxidant the more likely the formation of quinone.

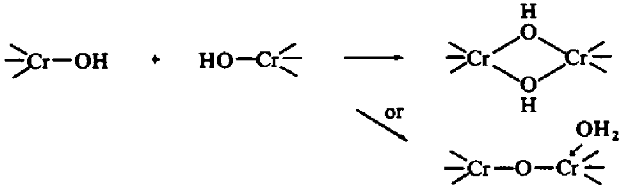
In the phenoxy radical the spin density is highest at the *ortho* and *para* positions.[6] Thus electrophilic attack is more likely at these positions than at the *meta* position so that side chains at the *ortho* positions are more likely to be attacked than equivalent side chains at the *meta* positions. Also, *ortho* side chains with α hydrogen are more likely to undergo attack than those without such hydrogens. If side chain attack is important it could explain how 3,5-dialkyl phenols can give more quinone than the 2,6- analogues and how the t-butyl phenols give higher yields than their Me analogues. At high oxidant to phenol ratios, that is under conditions in which the possibility of coupling reactions occurring has been minimized, this behaviour is observed. The nature of the side chain attack has not been determined but possible products are aldehydes[23] or quinone methides. The formation of the latter could take place as illustrated below.



The polymerization and other reactions of these quinone methides have been discussed by Turner.[24]

The high yield of quinone given by 2,5-di-t-butylphenol can be explained in terms of resistance to side chain attack and steric hindrance to coupling. The t-butyl in the 5 position would make coupling in the 4 and 6 positions very difficult but would not offer resistance to the further oxidation of the radical to quinone.

The final stage of the reaction, namely the formation of the solid, is probably a complex condensation reaction in which the OH groups on the different chromium atoms interact. In this way both Cr (III) and Cr (V) would be precipitated.



That both quinones and other organic products are only released on the hydrolysis of the adduct is hardly surprising since the oxidized organic compounds all contain oxygen which would function as the ligand atom towards the various chromium species present.

EXPERIMENTAL

The phenols were purified by recrystallization or fractional distillation. The CrO_2Cl_2 was purified by room temp distillation at reduced press immediately prior to use. The CCl_4 was dried by shaking with P_2O_5 followed by fractional distillation.

The oxidation reactions were carried out by adding the phenol, in a large excess of dry CCl_4, slowly to a vigorously stirred soln of the CrO_2Cl_2 in CCl_4. In all the reactions studied, a solid precipitated out after the first few drops of phenol had been added. After the completion of the phenol addition the mixture was stirred for a further hr then filtered using an enclosed filter. The solid was washed with portions of dry solvent until free from excess CrO_2Cl_2 and was dried at room temp under reduced press. The solid was

TABLE 1

	Mole ratio	% substituted *p*-benzoquinone	Other products
Phenol	CrO_2Cl_2 to ArOH		
o-Cresol	2:1	1	tar
2,6-Dimethyl	2:1*	48·3	10·3% 33'55' tetra methyl diphenoquinone
	10:1	16·4	4·7% 33' 55' tetra methyl diphenoquinone
2,6-Di-t-butyl	1·3:1	36·0	
	2:1*	68·5	Traces of 33'55' tetra-t-butyl diphenoquinone
	5:1	58·0	
2,5-Dimethyl	2:1	14·5	Polymeric tars one component with molecular weight 312
	5:1*	15·5	
2,5-Di-t-butyl	1:1	27·8	
	1·3:1	75·0	
	2:1*	82·7	
	5:1	76·1	
	10:1	62·8	
3,5-Dimethyl	2:1	4·8	From tar was obtained a small quantity of a solid with molecular weight. 362·188 and molecular formula $C_{24}H_{26}O_3$
	7:1	19·4	
	100:1*	22·6	
3,5-Di-t-butyl	2:1	30·7	
	5:1	49·0	Polymeric tar
	10:1*	56·7	

* Mole ratio giving best yield of quinone.

hydrolysed by addition to a large volume of cold water. The hydrolysis of the t-butyl derivatives gave immediate precipitation of quinone but for the Me derivatives no quinone was obtained at this stage although the 2,6-dimethylphenol derivative gave some diphenoquinone. The hydrolysis soln was then extracted with organic solvents such as ether and $CHCl_3$. Evaporation of solvent from the extract gave the quinone (often very impure). Purification was effected by recrystallization and sublimation. The purity was checked by comparison with literature m.ps and IR spectra. Mol wts were confirmed by mass spectra measurements.

Table 1 summarizes the yields of quinones obtained.

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