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# THE OXIDATION OF PHENOLS WITH CHROMYL CHLORIDE—I

## PHENOL, CHLOROPHENOLS AND RELATED PHENOXYTRICHLOROSILANES

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**Abstract**—The reactions of chromyl chloride with various phenolic compounds yield brown solids which in general do not have stoichiometric composition. The hydrolysis of these solids gives varying yields of the *p*-benzoquinones. The presence of chlorine in the positions *ortho* to the phenolic oxygen results in increased yields of the quinone.

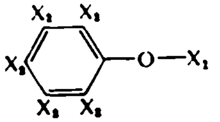
## DISCUSSION

CHROMYL chloride has been used for the oxidation of organic compounds for many years. The reactions investigated prior to 1957 were the subject of a review,[1] and more recent progress in this field has been discussed by Wiberg.[2]

The reaction which has attracted the most attention involves the conversion of toluene to benzaldehyde. The nature of the adduct formed in the toluene–chromyl chloride reaction has been the subject of much speculation[1–5] but there is as yet no definite description of this compound. The most recent evidence[6] relating to the structure of the adduct indicates that is is a co-ordination complex containing benzaldehyde co-ordinated onto chromium; magnetic susceptibility and ESR measurements indicate that the chromium is present as Cr(IV).[2]

The preparations of benzoquinones are well documented.[7] Chromyl chloride has been used to obtain certain quinones from aromatic hydrocarbons.[8] Fremy's salt[9] and lead dioxide[10] are amongst the more recently introduced reagents used for the oxidation of phenols to quinones.

We have investigated the reactions of chromyl chloride with compounds of the type



where $X_1$ is —H or --$SiCl_3$ and $X_2$ is —H or —Cl.

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[1] W. H. Hartford and M. Darrin. *Chem. Rev.* 58, 1 (1958).

[2] K. B. Wiberg. *Oxidation in Organic Chemistry.* Academic Press (1965).

[3] O. H. Wheeler. *Canad. J. Chem.* 38, 2137 (1960).

[4] I. Necsoui, A. J. Balaban, I. Pascaru, E. Sliam, M. Eliam and C. D. Nenitzescue. *Tetrahedron* 19, 1113 (1963).

[5] K. B. Wiberg and R. Eisenthal. *Tetrahedron* 20, 1151 (1964).

[6] H. C. Duffin and R. Tucker. *Chem. & Ind.* 1262 (1966).

[7] J. Cason. *Organic Reactions.* Vol. IV; p. 305. Wiley, N.Y. (1948).

[8] O. H. Wheeler. *Canad. J. Chem.* 36, 949 (1958).

[9] H. J. Teuber and W. Rau. *Chem. Ber.* 86, 1036 (1953).

[10] M. Hedayatullah and L. Denivelle. *C.R. Acad. Sci., Paris* 254, 2369 (1962).

These reactions, carried out in a large excess of dry carbon tetrachloride, give brown solids, the compositions of which do not correspond to definite adducts. The solids, on hydrolysis, give either tar or quinone. Substitution of chlorine for hydrogen in the 2 and 6 positions leads to a considerable increase in the yield of quinone. Thus, while 2,6-dichlorophenol and 2,4,6-trichlorophenol give good yields of 2,6-dichloro-*p*-benzoquinone and pentachlorophenol gives a yield of chloranil in excess of 70%, *o*-chlorophenol gives only a very small yield of 2-chloro-*p*-benzoquinone and phenol itself gives only traces of *p*-benzoquinone.

The nature of the solids formed in the initial reaction has yet to be elucidated: the composition and nature of hydrolysis products point to their being mixtures. The IR spectra of most solids show few well defined features beyond strong bands in the 3300–3500 cm$^{-1}$ and 1600–1700 cm$^{-1}$ regions. There are exceptions to this rule; the solids derived from 2,4,6-trichlorophenol and pentachlorophenol show absorption bands similar to those described for the benzoquinones[11] formed on hydrolysis. This evidence would seem to point to the presence of the quinone in the solid. Further pieces of evidence leading to the same conclusion are the ease of removal of the chloranil from the pentachlorophenol solid: it can be removed by washing with hot dry carbon tetrachloride, and, the removal of 2,6-dichloro-*p*-benzoquinone from the 2,4,6-trichlorophenol solid by vacuum sublimation.

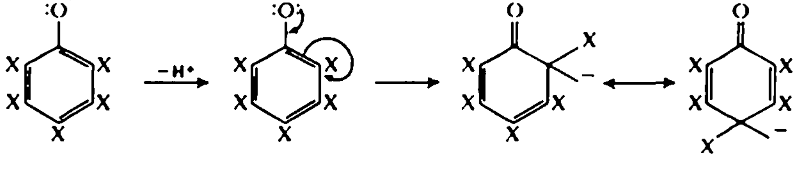
In the latter case it should be pointed out that although the 2,6-dichloro-*p*-benzoquinone is more soluble than the chloranil it cannot be removed by washing with hot carbon tetrachloride; the quinones could not be removed from any of the other solids prior to hydrolysis.

The firm adherence of the quinone to the solid indicates that it is bonded chemically rather than present as a mixture. The mode of attachment is not obvious. Extending the conclusions of Duffin and Tucker,[6] the solid could be described as a co-ordination complex of the quinone in which the carbonyl oxygen acts as the ligand atom. $>C{=}O \dashrightarrow Cr$. There are, however, some examples of quinone sandwich complexes with transition metals in ion oxidation states:[12] the solids prepared by us could be further examples of this type of compound but this is unlikely in view of the high oxidation state of the chromium.

A mechanism for the oxidation of phenols to quinones with Fremy's salt has been presented by Teuber;[9] a similar mechanism could be used to explain the reactions occurring in the systems studied by us.

The reaction can be conveniently split into 3 stages as follows.

I. The formation of the semiquinone:



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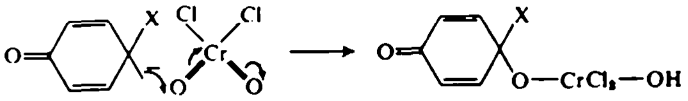
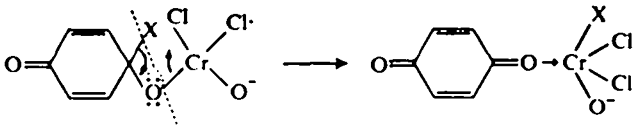
[11] F. E. Pritchard. *Spectrochim. Acta* **20**, 127 (1964).

[12] G. N. Schrauzer and H. Thyret. *J. Am. Chem. Soc.* **82**, 6420 (1960); *Z. Naturforsch.* **17b**, 73 (1962).

II. The electrophilic attack of the semiquinone by the chromyl chloride:



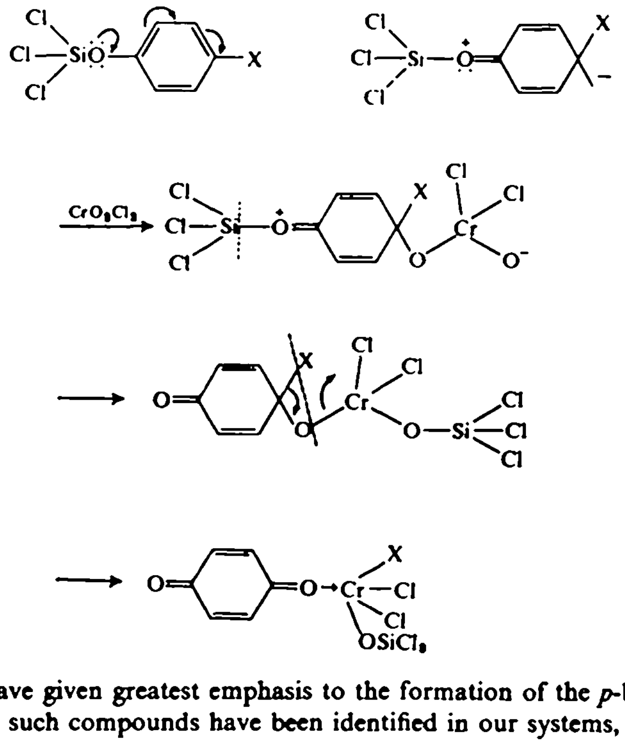
III. The rearrangement of the ester to give the quinone:



Similar processes could be written for stages II and III in which the other semiquinone is converted to the orthoquinone.

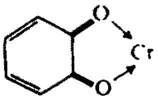
For compounds in which X = H further reaction or rearrangement is likely but until definite evidence of structure is available no mechanism can be postulated for this process.

The phenoxytrichlorosilanes require a modified scheme outlined below:

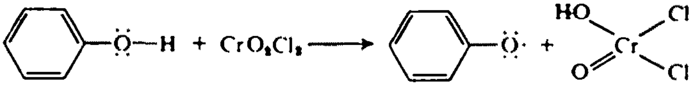


While we have given greatest emphasis to the formation of the *p*-benzoquinone, mainly because such compounds have been identified in our systems, the formation of the *o*-benzoquinones cannot be excluded. In many systems brown and red tars were formed as a result of the hydrolysis reaction and such tars could well arise from the decomposition of the *o*-benzoquinones.

The firm adherence of the organic matter to the chromium would be better explained by *o*-benzoquinone formation as this compound could function as a chelating agent towards the chromium, but as yet these is no evidence of *o*-benzoquinone formation.



An alternative explanation of the tar formation could be free radical formation during the first stage of oxidation, and coupling of the free radicals to form polymers.[13]



## EXPERIMENTAL

The phenols were purified by recrystallization or fractional distillation. The phenoxytrichlorosilanes were prepared by heating the appropriate phenol, dissolved in benzene with a fivefold excess of $SiCl_4$: purification was effected by fractional distillation. The chromyl chloride was used as supplied by Messrs. Hopkin and Williams, unless analysis indicated it to be impure, in which case it was purified by fractional distillation. The $CCl_4$ was purified by fractional distillation.

In each of the reactions studied the following procedure was used. The chromyl chloride in a large excess of dry $CCl_4$ was added slowly to a well stirred soln of the phenol, or phentoxytrichlorosilane, in a large excess of dry $CCl_4$.

The mixture was stirred, or shaken for a further 2 hr, and then filtered through a sintered glass filter suitably protected from the atmosphere. After washing the solid with dry $CCl_4$ final traces of solvent were removed under reduced press. The IR spectra of the solids were recorded in Nujol mulls using a Grubb Parsons Spectromaster. These mulls were prepared in a dry atmosphere.

The solids were hydrolysed under a variety of conditions. For the solids derived from the dichloro, trichloro and pentachlorophenols and the solids derived from the dichlorophenoxy- and trichlorophenoxytrichlorosilanes, the hydrolysis was performed by adding the solid to a large excess of water, filtering off quinone so formed and extracting further quantities of quinone from the aqueous soln with ether or $CCl_4$. For the solids derived from the phenols, or phenoxytrichlorosilanes containing fewer than two chlorines attached to the ring, the above procedure gave only brown or red brown tars. Where only a tar could be obtained, hydrolysis with hydrated $Na_2CO_3$ or hydrated $MgSO_4$ was tried. By heating a mixture of the solid and hydrated salt in $CCl_4$ it was sometimes possible to isolate small quantities of quinone.

*Phenol* (18·8 g, 1 mole )and chromyl chloride (31·0 g, 1 mole) gave a brown solid (45·7 g), (Found: C, 28·2; Cl, 32·0; Cr, 17·8: Calc. for 1:1 adduct: C, 28·9; Cl, 28·5; Cr, 20·9%.) Hydrolysis of this solid yielded a dark brown tar from which only traces of *p*-benzoquinone could be obtained.

*o-Chlorophenol* (4·10 g, 1 mole) and chromyl chloride (6·70 g, 1·33 moles) gave a brown solid (10·55 g), (Found: C, 20·3; Cl, 35·7; Cr, 18·4: Calc. for 1:1 adduct: C, 25·4; Cl, 37·6; Cr, 25·4%.) Hydrolysis of the solid gave a brown tar from which 2-cholro-*p*-benzoquinone was obtained on vacuum sublimation. The yield of quinone obtained was approximately 15%.

2,6-*Dichlorophenol* (12·70 g, 1 mole) and chromyl chloride (12·10 g, 1 mole) gave a brown solid (20·6 g), (Found: C, 22·2; Cl, 47·2; Cr, 16·2; Calc. for 1:1 adduct: C, 22·6; Cl, 44·6; Cr, 16·3%.) Hydrolysis of samples of the solid gave 2,6-dichloro-*p*-benzoquinone in yields of approximately 40%.

2,4,6-*Trichlorophenol* (19·75 g, 1 mole) and chromyl chloride (15·50 g, 1 mole) gave a brown solid (28·65 g), (Found: C, 20·3; Cl, 47·5; Cr, 14·6. Calc. for 1:1 adduct: C, 20·4; Cl, 50·4; Cr, 14·7%.) Hydrolysis or vacuum sublimation of samples of the solid gave 2,6-dichloro-*p*-benzoquinone in yields of 55–60%.

*Pentachlorophenol* (13·40 g, 1 mole) and chromyl chloride (7·7 g, 1 mole) gave a brown solid (15·44 g), (Found: C, 17·0; Cl, 57·6; Cr, 12·8. Calc. for 1:1 adduct: C, 17·1; Cl, 59·0; Cr, 12·3%.)

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[13] A. I. Scott. *Quart. Rev.* XIX, 1 (1965).

Hydrolysis, or extraction with hot $CCl_4$ of samples of the solid, gave chloranil in yields between 70 and 80%.

*Phenoxytrichlorosilane* (22·7 g, 1 mole) and chromyl chloride (15·1 g, 1 mole) gave a dark brown solid (29·6 g), (Found: C, 15·7; Cl, 46·2; Cr, 16·9. Calc. for 2 silane–3 chromyl chloride adduct; C, 15·6; Cl, 46·3; Cr, 16·9%.) Hydrolysis of the solid gave a dark brown tar.

o-*Chlorophenoxytrichlorosilane* (26·2 g, 1 mole) and chromyl chloride (15·5 g, 1 mole) gave a brown solid (27·0 g), (Found: C, 14·2; Cl, 48·0; Cr, 15·6. Calc. for 2 silane–3 chromyl chloride adduct; C, 14.6; Cl, 50·25; Cr, 15·8%.) Hydrolysis of this solid gave a tar.

2,6-*Dichlorophenoxytrichlorosilane* (5·93 g, 1 mole) and chromyl chloride (7·75 g, 1 mole) gave a light brown solid (8·65 g), (Found: C, 16·1; Cl, 46·9; Cr, 17·5. Calc. for 2 silane–3 chromyl chloride adduct: C, 13·6; Cl, 53·5; Cr, 14·7%.) Hydrolysis of samples gave only one organic product—2,6-dichloro-*p*-benzoquinone.

2,4,6-*Trichlorophenoxytrichlorosilane* (3·31 g, 1 mole) and chromyl chloride (7·75 g, 2 moles) gave a light brown solid (4·13 g), (Found C, 15·7; Cl, 47·0; Cr, 17·0. Calc. for 2 silane–3 chromyl chloride adduct: C, 12·7; Cl, 56·5; Cr, 13·8%.) Hydrolysis gave only 2,6-dichloro-*p*-benzoquinone.

The bands in IR spectrum of the trichlorophenol solid are tabulated below, together with those for the partially hydrolysed solid and for the pure 2,6-dichloro-*p*-benzoquinone.

| | (Frequencies in $cm^{-1}$) | | |
|---|---|---|---|
| Solid-product | Solid after exposure to the atmosphere | 2,6-dichloro-*p*-benzoquinone | Assignment[11] |
| 1694 v.s. | 1702 v.s. | 1698 v.s. | $\nu$ (C=O) adjacent to C—Cl |
| 1661<br>1627<br>1600 very broad v.s. | 1661<br>1652<br>1639 very broad v.s. | 1661<br>1653<br>1648 v.s. | $\nu$ (C=O) adjacent to C—H |
| 1574 v.s. | 1587 v.s. | 1586 s. | $\nu$ (C—C) |
| | 1510 m. | | |
| 1330 sh. | 1324 v.s. | 1330 sh. | $\nu$ (C—C) |
| | 1294 v.s. | 1293 m. | $\nu$ (C—C) |
| 1282 m. | 1281 v.s. | 1278 v.s. | $\beta$ (C—H) |
| 1255 m. | | | |
| 1050 v.s. | 1038 v.s. | 1038 v.s. | $\beta$ (C—H) |
| 904 v.s. | 907 v.s. | 913 v.s. | $\gamma$ (C—H) |
| 790 v.s. | 795 s. | 800 s. | $\gamma$ (C—H) |
| 781 v.s. | 781 v.s. | 781 v.s. | Ring breathing. |

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