

The Synthesis and Oxidation of Certain Perchlorylbenzenes

DAVID M. GARDNER, ROBERT E. OESTERLING, AND FRANCIS L. SCOTT

Research and Development Department, Pennsalt Chemicals Corporation, Wyndmoor, Pennsylvania

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Perchlorylbenzene and several of its derivatives have been subjected to a variety of strong oxidizing agents with either no reaction or the formation of products still containing the $-\text{ClO}_3$ group. The explosive diperchloryldiphenoquinone, m.p. 180–182°, is the first known compound with the $-\text{ClO}_3$ group attached to other than the benzene ring. The acidities of 3-perchlorylphenol and 4-perchlorylphenol were measured at 30° in aqueous solution and the apparent $\text{p}K_a$ values were determined as 8.00 and 7.62, respectively.

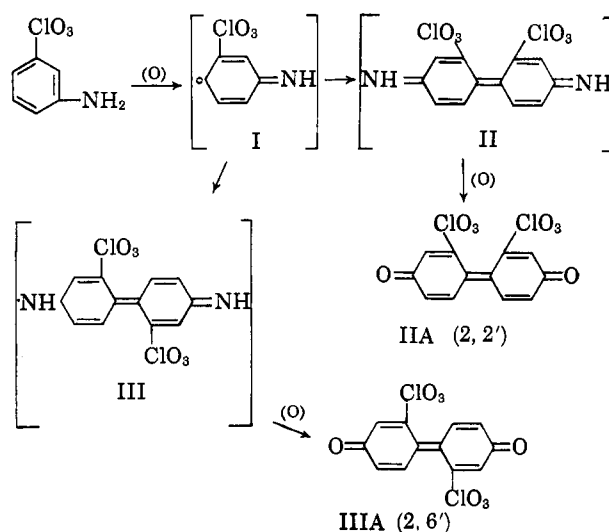
The general synthesis and some reactions of perchlorylbenzenes have been reported previously^{1–3} by this laboratory. A study of the effects of selected strong oxidizing agents on perchlorylbenzene, perchloryltoluene, perchlorylphenol, perchlorylaniline, and fluoroperchlorylbenzene has indicated that the $-\text{ClO}_3$ group is resistant to oxidation. Products resulting from these oxidation reactions originate either by attack of the oxidizing agents on substituent groups on the perchlorylbenzene nucleus or by substitution on the benzene ring itself.

Perchlorylbenzene was not affected by treatment with aqueous permanganate, acid dichromate, concentrated nitric acid, solutions of nitrosyl sulfate in sulfuric acid, or aqueous perchloric acid.

In contrast, an isomeric mixture of perchloryltoluenes was readily oxidized with aqueous permanganate to yield predominantly *p*-perchlorylbenzoic acid. It is interesting to note that alkaline hydrolysis of the perchloryltoluene mixture yielded cresols in approximately the following isomer mole ratios: 50% *meta*, 30% *para*, and 20% *ortho*. The cresol isomer distribution is puzzling since electrophilic substitution, as during the preparation of perchloryltoluene, normally favors the *para* position. Perhaps the best explanation for the predominance of *m*-cresol as a hydrolysis product is to assume that the hydrolytic deperchlorylation is not a simple displacement, but that it involves a benzyne intermediate.⁴ The isomer distribution in the cresols would thus be representative of the reactions of a mixture of 2- and 3-methyl substituted benzyne. The proportion of the *meta* isomer formed is in accord with that supposition.⁵

Oxidation of 3-perchlorylaniline with aqueous acid dichromate gave the explosive diperchloryldiphenoquinone. The latter compound is believed to be the first organic compound prepared with the $-\text{ClO}_3$ group attached to other than the benzene nucleus.

The formation of the diperchloryldiphenoquinone from 3-perchlorylaniline probably involves a quinone-imine intermediate I which may couple in two ways to give the 2,2'-isomer IIA or the 2,6'-isomer IIIA. We have not studied the product sufficiently to obtain evidence as to the way the coupling occurs. However, on the basis of steric considerations only, we have formulated the product as the 2,6'-isomer. For the opera-



tion of steric effects in the diphenoquinone series, see the work of Bourdon and Calvin.⁶

Since 3-perchlorylphenol was not oxidized by acid dichromate solution under the same conditions this compound and its unknown quinone derivative were not considered as possible intermediates in the oxidation mechanism of the 3-perchlorylaniline.

The quinone-imine intermediate I could polymerize (rather than dimerize) and, indeed, varying amounts of polymer (up to one-half the weight of crude product) were obtained in the experiments. The polymer was of indeterminate composition probably as a result of subsequent partial oxidation. However, it did contain nitrogen, and an infrared spectrum was similar to that for the diperchloryldiphenoquinone.

Diperchloryldiphenoquinone, unlike the parent molecule diphenoquinone,⁷ is not readily reduced to the corresponding dihydroxybiphenyl.

4-Fluoroperchlorylbenzene and 4-perchlorylphenol were easily nitrated to 3-nitro-4-fluoroperchlorylbenzene and 2,6-dinitro-4-perchlorylphenol, respectively. The latter compound is an analog of picric acid and is dangerously explosive.

An aqueous solution of 4-perchlorylphenol was titrated potentiometrically with base at 30° and, from the half-neutralization point, its $\text{p}K_a$ was determined to be 7.62. The $\text{p}K_a$ of 3-perchlorylphenol determined similarly was 8.00. Using these apparent ionization constants and the Hammett parameter, ρ , and other

(1) C. E. Inman, R. E. Oesterling, and E. Tyczkowski, *J. Am. Chem. Soc.*, **80**, 5286 (1958).

(2) F. L. Scott and R. E. Oesterling, *ibid.*, **82**, 5247 (1960).

(3) F. L. Scott and R. E. Oesterling, *J. Org. Chem.*, **25**, 1688 (1960).

(4) This possibility is being explored further by F. L. S.

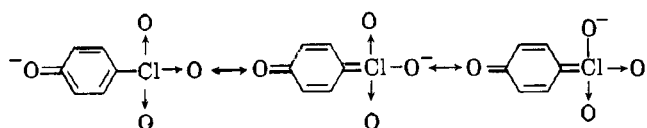
(5) See R. Huisgen, "Organometallic Chemistry," H. Zeiss, Ed., ACS Monograph no. 147, Reinhold Publishing Corp., New York, N. Y., 1960, pp. 77.

(6) J. Bourdon and M. Calvin, U. S. Atomic Energy Commission, UCRL-3466, 1956.

(7) R. Willstätter and L. Kalb, *Ber.*, **38**, 1232 (1905).

values for the phenol series,^{8,9} one can calculate that the substituent constant for a *para*-substituted $-\text{ClO}_3$ group, σ_p , is +1.07. For the *meta*-substituted $-\text{ClO}_3$ group one can calculate a value of +0.89 for the substituent constant, σ_m . Because aliphatic perchloryl compounds are to date unknown (to provide a measure of the inductive contribution, σ_i , to the substituent constant),¹⁰ one cannot resolve the contributions here due to resonance and polar effects. However, the following points suggest themselves.

We can use data available prior to this work to derive a σ_p for the perchloryl group. Thus it is reported¹ that the nuclear magnetic shielding parameter, δ^F , for the F^{19} n.m.r. absorption in *p*-fluoroperchlorylbenzene is +1.26. If we now use the data reported by Gutowsky¹¹ and replot his graph of σ vs. δ (despite Taft's¹⁰ legitimate criticism of the lack of precise correlation of the plot), we can derive an interpolated σ_p value for the perchloryl group of +0.98. Coincidentally, this is midway between the σ_p and σ_m values for the perchloryl group calculated from our new data. We might indicate that the δ^F value for *p*-chlorosulfonyl ($-\text{SO}_2\text{Cl}$) is also +1.26. This implies an electronic and perhaps a steric resemblance between the perchloryl and sulfonyl groups. Secondly, taking the $\text{p}K_a$'s (at 25°) of 3-nitrophenol as 8.38 and of 4-nitrophenol as 7.15,¹² our data suggest that with regard to inductive effects, broadly speaking, *m*- $\text{ClO}_3 > m\text{-NO}_2$, and that with regard to resonance effects *p*- $\text{NO}_2 > p\text{-ClO}_3$. This relative order is supported by the fact that 4-nitrofluorobenzene reacts more rapidly with methoxide ion than does 4-fluoroperchlorylbenzene. Finally, the increase in acidity on going from 3-perchlorylphenol to 4-perchlorylphenol¹⁴ indicates that in the latter compound the perchloryl group can sustain some degree of negative charge through resonance.



Perchlorylbenzene and its derivatives, particularly those containing additional oxidizer substituents on the benzene nucleus, are explosive materials of high brisance and are quite sensitive to shock, friction, and high temperatures. It is mandatory that one use caution and utmost safety in preparing and handling these compounds.

(8) A. I. Biggs and R. A. Robinson, *J. Chem. Soc.*, 388 (1961), use a ρ value for the phenol series of 2.229 and a $\text{p}K_a$ for phenol itself at 25° of 9.998.

(9) M. M. Fickling, A. Fischer, B. R. Mann, J. Packer, and J. Vaughan, *J. Am. Chem. Soc.*, **81**, 4226 (1959), use a ρ value of 2.183.

(10) R. W. Taft, Jr., *ibid.*, **79**, 1045 (1957), and subsequent papers by this author and his group.

(11) H. S. Gutowsky, V. W. McCall, B. P. McGarvey, and L. H. Meyer, *ibid.*, **74**, 4809 (1952).

(12) In our calculations of the σ values for the perchlorylphenols and in the comparisons of these $\text{p}K_a$'s with those of the nitrophenols we have used the literature data determined at 25°. In the case of 4-nitrophenol, for example, adjustment of its $\text{p}K_a$ from 25° to 30°, involves a change in $\text{p}K_a$ from 7.15 to 7.10.¹³ This corresponds to a change of about 1%.

(13) G. F. Allen, R. A. Robinson, and V. E. Bower, *J. Phys. Chem.*, **66**, 171 (1962).

(14) The σ values involved imply a "dual" perchloryl value similar to those ascribed to *p*-nitro, etc. There has been recent criticism [see H. vanBekkom, P. E. Verkade, and B. M. Wepster, *Rec. trav. chim.*, **78**, 815 (1959)] of this approach, and it is apparent that there is in reality a continuum of σ_p values for any one substituent. Because of the lack of a variety of pertinent perchloryl aromatic compounds, we are unable to make any further addition to the σ picture for $-\text{ClO}_3$ other than the values reported here.

Experimental

3-Perchlorylphenol.—A solution of 6.36 g. (30 mmoles) of 3-perchlorylaniline hydrochloride, prepared according to the procedure of Inman, *et al.*,¹ was diazotized at 0° in 25 ml. of 18% hydrochloric acid using 2.76 g. (40 mmoles) of sodium nitrite. The clear yellow solution of diazonium salt, was added slowly to 100 ml. of boiling 50% sulfuric acid containing 50 g. of copper sulfate. The resulting solution was steam distilled and the distillate was extracted with ether. The dried ethereal extracts yielded 4.2 g. (80% crude yield) of a heavy red oil on evaporation. Vacuum distillation, 100° (0.01 mm.), of the crude material in a molecular still gave a pale yellow oil which crystallized in the receiver. After recrystallization from benzene-petroleum ether this was obtained as colorless needles, m.p. 43–45°.

Anal. Calcd. for $\text{C}_6\text{H}_5\text{ClO}_4$: C, 40.81, H, 2.85; Cl, 20.08; neut. equiv., 176.6. Found: C, 40.58; H, 3.22; Cl, 20.10; neut. equiv., 179.

The infrared spectrum shows a pattern between 860 and 722 cm^{-1} characteristic of *meta*-substituted benzenes. A strong absorption band at 1198–1190 cm^{-1} is typical of the perchloryl group and is assigned to the Cl—O stretching frequency. Multiple absorptions are observed for the phenolic group in the 3650–3330- cm^{-1} region.

The proton n.m.r. spectrum shows a very unsymmetrical pattern for the aromatic protons. The spectrum indicates, at moderate resolution, essentially three environmentally dissimilar protons which, when considered with peak heights or abundance, is consistent with *meta* substitution.

4-Perchlorylphenol.—A solution of 26.4 g. (0.148 mole) of 4-fluoroperchlorylbenzene dissolved in 50 ml. of dry methanol was added, at room temperature, to a solution of sodium methoxide in methanol prepared by reacting 3.6 g. (0.158 g.-atoms) of sodium with 500 ml. of methanol. The mixture was allowed to stand overnight then refluxed for 5 hr. The mixture was cooled, added to 400 ml. of ether, and washed with several 100-ml. portions of water. The ethereal solution was dried and evaporated to give 28 g. of crude 4-methoxyperchlorylbenzene. Vacuum distillation [83–85° (0.1 mm.)] gave 21 g. (0.11 mole, 74% yield) of pure product, n_D^{25} 1.5323.

Anal. Calcd. for $\text{C}_6\text{H}_7\text{ClO}_4$: C, 44.11; H, 3.70; Cl, 18.60. Found: C, 44.4; H, 3.8; Cl, 18.5.

4-Methoxyperchlorylbenzene (10 g., 52 mmoles) was added to 125 ml. of constant boiling hydriodic acid and the mixture was refluxed for 3 hr. The initial temperature was 126°, and this gradually diminished to 119° during the reaction. The mixture was cooled and diluted with 500 ml. of water and the free iodine was reduced by stirring in solid sodium bisulfite. The aqueous solution was extracted with three 100-ml. portions of ether and the dried ethereal extracts were evaporated to yield 6.5 g. of crude product. Vacuum distillation [50° (0.1 mm.)] served to separate 2.5 g. (26 mmoles, 50% yield) of phenol which crystallized in the condenser.¹⁶ The residue, 4.0 g. (23 mmoles, 43.5% yield), was recrystallized from benzene-petroleum ether to give colorless needles of 4-perchlorylphenol, m.p. 83–84°.

Anal. Calcd. for $\text{C}_6\text{H}_5\text{ClO}_4$: C, 40.81; H, 2.85; Cl, 20.08; neut. equiv., 176.6. Found: C, 40.73; H, 2.45; Cl, 20.35; neut. equiv., 177.6.

The infrared spectrum shows characteristic perchloryl and hydroxyl absorption bands at 1190 cm^{-1} and in the 3300 cm^{-1} region, respectively. In addition, absorption at 833 cm^{-1} is observed denoting *para* substitution.

The proton n.m.r. spectrum shows peaks for the aromatic protons which are in a symmetrical pattern and indicative of two environmentally dissimilar protons. This is consistent with *para* substitution.

Perchloryltoluene.—The preparation followed the general procedure previously described for perchlorylbenzene derivatives.¹ Perchloryl fluoride gas was passed slowly through a suspension of 80 g. of anhydrous aluminum chloride in 200 ml. of toluene at 0°–15°. The mixture became black almost immediately and hydrogen chloride was evolved. After 6 hr. the rate of hydrogen chloride evolution became negligible and the reaction was terminated. The mixture was filtered and the clear filtrate was steam distilled. The toluene layer in the distillate was separated,

(15) The formation of phenol is a result of two processes: (1) the cleavage of the methoxy group; and (2) a hydrogen iodide induced deperchlorylation. We cannot comment on the relative rates of these reactions but the reductive deperchlorylation is very similar to that realized in the hydrogenolysis of the perchlorylaromatic compounds.⁸

dried, and evaporated to give 98.7 g. of crude product. Vacuum distillation [65–78° (0.3 mm.)] gave an isomeric mixture of perchloryltoluenes.

A sample of 1.7 g. (10 mmoles) of the isomeric mixture of perchloryltoluenes was hydrolyzed by refluxing for 16 hr. with 50 ml. of 50% aqueous ethanol containing 1.4 g. (25 mmoles) of potassium hydroxide. The mixture was cooled, extracted with ether, and the ether layer was dried and evaporated to give 1.05 g. (9.7 mmoles, 97% yield) of isomeric cresols. Examination of the infrared spectrum of the cresols indicated the following isomer mole ratios: 50% *meta*, 30% *para*, and 20% *ortho*. This estimate was based on a study of the relative infrared absorption intensities at 750, 770, and 817 cm^{-1} .

The original perchloryltoluene mixture was not further studied save that it was used in the following oxidation experiment.

Perchlorylbenzoic Acid.—To 200 ml. of water was added 5.0 g. (29 mmoles) of the isomeric perchloryltoluenes and the mixture was brought to reflux temperature. To it was added 400 ml. of a 4% aqueous potassium permanganate solution dropwise over a period of 1 hr. An additional 100 ml. of the permanganate solution was added in one increment and the mixture was stirred at reflux for an additional hour. The hot mixture was treated with sulfur dioxide gas to reduce the excess permanganate and filtered. The aqueous solution was cooled to 0° and filtered to give 1.9 g. of a white granular solid.

Extraction of the aqueous filtrate with ether gave, upon drying and evaporation of the ether, an additional 1.1 g. of product or a total of 3.0 g. (50% yield) of perchlorylbenzoic acid. Recrystallization from hot water gave colorless granular crystals of pure perchlorylbenzoic acid.

Analysis of the water filtrate after extraction with ether showed chloride ion present indicating hydrolysis of the perchloryl group to the extent of 17% of the starting material as a competing side reaction.

The perchlorylbenzoic acid decomposes on heating at 250–280° and no melting point is detectable.

Anal. Calcd. for $\text{C}_7\text{H}_3\text{ClO}_5$: C, 41.09; H, 2.46; Cl, 17.33; neut. equiv., 205. Found: C, 41.20; H, 2.48; Cl, 17.18; neut. equiv., 203.

The infrared spectrum shows absorption at 1698 and 2500 cm^{-1} (broad band) typical of the $-\text{COOH}$ group and dimerization through the carboxylic group. *para* Substitution is evident by a strong band at 855 cm^{-1} and a very much weaker absorption band at 762 cm^{-1} can be assigned to *meta* and/or *ortho* substitution effects.

Attempted Oxidation of Perchlorylbenzene.—Separate 1.6-g. samples of perchlorylbenzene were treated with the following oxidizing agents at the temperatures and for the times noted. In each experiment the only organic product isolated was unchanged perchlorylbenzene: 3.0 g. of potassium permanganate in 50 ml. of water (100°, 3 hr.); 6.0 g. of sodium dichromate in 100 ml. of 10% sulfuric acid (100°, 3 hr.); 50 ml. of 70% nitric acid (70–80°, 3 hr.); 2.36 g. of dinitrosyl pyrosulfate in 5 ml. of concentrated sulfuric acid (100°, 1 hr.); 3.0 g. of 72% perchloric acid (100°, 1 hr.)

3-Nitro-4-fluoroperchlorylbenzene.—A solution of 3.1 g. of concentrated nitric acid in 100 ml. of concentrated sulfuric acid was added dropwise to a solution of 5.0 g. (28 mmoles) of 4-fluoroperchlorylbenzene dissolved in 30 ml. of concentrated sulfuric acid. The temperature rose to about 35° during the addition. The mixture was warmed to 50° for 1 hr. and then to 60° for an additional hour. The reactants were cooled and poured over ice. A yellow oil separated which was washed with water and dried over magnesium sulfate. Molecular distillation gave 5.0 g. (22 mmoles, 78.6% yield) of 3-nitro-4-fluoroperchlorylbenzene, n_D^{25} 1.5374, which slowly crystallized on standing, m.p. 43–45°.

Anal. Calcd. for $\text{C}_6\text{H}_3\text{ClFNO}_5$: C, 32.23; H, 1.35; N, 6.27. Found: C, 32.33; H, 1.49; N, 6.13. The infrared spectrum indicates 1,3,4-substitution in the benzene ring by absorption bands at 837, 877, and 885 cm^{-1} . Absorption at 1351 and 1548 cm^{-1} is typical of a nitro group substituent and absorption at 1205 cm^{-1} indicates the presence of the $-\text{ClO}_3$ group.

3-Nitro-4-fluoroperchlorylbenzene did not undergo further nitro group substitution on refluxing with 70% nitric acid at 70–80° for 4 hr.

2,6-Dinitro-4-perchlorylphenol.—4-Perchlorylphenol (0.5 g., 2.8 mmoles) was added to 20 ml. of concentrated nitric acid and the mixture was refluxed at 70–80° for 3 hr. The mixture was then cooled and poured over ice. The resulting aqueous solution was extracted with ether and the ethereal solution was dried and evaporated to give 0.65 g. (2.4 mmoles, 86% yield) of crude 2,6-dinitro-4-perchlorylphenol. The pure material was obtained as a yellow granular solid, m.p. 105–107° (135° dec., with gassing), following recrystallization from a mixed chloroform-petroleum ether solvent. This material is dangerously explosive and is especially sensitive to shock.

Anal. Calcd. for $\text{C}_6\text{H}_3\text{ClN}_2\text{O}_8$: C, 27.02; H, 1.13; N, 10.51; neut. equiv., 266.5. Found: C, 27.16; H, 1.36; N, 10.30; neut. equiv., 268.

2,6-Dinitro-4-perchlorylphenol, dissolved in ether, readily formed a salt with triethylamine. The yellow crystals, m.p. 100–102°, were filtered off and dried.

Anal. Calcd. for $\text{C}_{12}\text{H}_{15}\text{N}_3\text{ClO}_8$: N, 11.44. Found: N, 11.84.

Other Attempted Oxidations of 4-Perchlorylphenol.—The reaction of 0.1 g. of 4-perchlorylphenol with 1.0 g. of dinitrosyl pyrosulfate in 2 ml. of concentrated sulfuric acid at 100° resulted in complete degradation of the perchlorylphenol and formation of a black carbonaceous residue.

An unusual reaction was observed on treating 0.5 g. of perchlorylphenol with 5 ml. of 72% perchloric acid. At a temperature of 85° the reaction became strongly exothermic and the temperature rose to 135°. The only product isolated was 0.1 g. of tetrachloroquinone, identified by its infrared spectrum.

2,6'-Diperchlorylidiphenoquinone.—3-Perchlorylaniline hydrochloride (1.1 g., 5 mmoles) was dissolved in 30 ml. of 25% sulfuric acid and a solution of 2.5 g. of sodium dichromate in 15 ml. of water was added with stirring at 0°. Stirring was continued for 5 hr. at 0° and the mixture was filtered to give 0.7 g. of brown solid which was extracted with chloroform.

The residual insoluble, brown-red polymeric material was high melting and explosive. Elemental analyses indicated 5.87% nitrogen and 12.65% chlorine (calcd. for structure I: N, 8.02; Cl, 20.34). Apart from broader and less distinct bands typical of a high molecular weight polymer, the infrared absorption spectrum was very similar to that found for 2,6'-diperchlorylidiphenoquinone.

The clear chloroform extract was evaporated to one-half its volume, petroleum ether was added until a precipitate formed, and the solution was chilled to 0° to give 0.45 g. (1.3 mmoles, 52% yield) of light orange crystals of 2,6'-diperchlorylidiphenoquinone. Final purification was by recrystallization from carbon tetrachloride. The material has m.p. 180–182°, is shock sensitive, and undergoes decomposition at 250°.

Anal. Calcd. for $\text{C}_{12}\text{H}_8\text{Cl}_2\text{O}_8$: C, 41.28; H, 1.73; Cl, 20.31; mol. wt., 349.1. Found: C, 41.41; H, 1.84; Cl, 20.49; N, none found; mol. wt., 359 (cryoscopic). The infrared spectrum shows $-\text{ClO}_3$ absorption bands at 1191 cm^{-1} , and strong bands at 1690 cm^{-1} , and 1590 cm^{-1} which have been assigned to the quinone carbonyl absorption and a coupling of the quinone carbonyl and the polycyclic ring absorptions.¹⁶

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(16) R. Hadzi and N. Sheppard, *J. Am. Chem. Soc.*, **73**, 5460 (1951).