Aryl pseudohypochlorites - some reactions with Lewis acids

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ARYL PSEUDOHYPOCHLORITES - SOME REACTIONS WITH LEWIS ACIDS.

A thesis presented to the Committee on Graduate Studies and the Department of Chemistry of Union College, Schenectady, New York, in partial fulfillment of the requirements for the degree of Master of Science.

By Frederick Charles Schwab 1966
acknowledgements

The author is deeply indebted to Professor William B. Martin, Jr. for his inspirational guidance, invaluable advice and criticism during the course of this investigation. The author would like to acknowledge the assistance of Mr. D. L. Harms and Miss Betty Toomey of the General Electric Materials and Processes Laboratory for their determination and interpretation of the infrared spectra, and the assistance of Mr. D. L. Chase for X-ray emission work. The author also gratefully acknowledges the cheerful assistance of his wife, Ilona, in helping to prepare this manuscript.
Several aryl hypochlorites were prepared by the action of chlorine on the sodium salts of substituted phenols. Infrared and ultraviolet spectral data confirmed a rearrangement of the resulting hypochlorites into ortho and para quinoid forms.

Friedel-Crafts reactions were carried out with the pseudohypochlorites and either benzene or anisole. Aluminum chloride was used as the catalyst. Analysis of these reactions showed two concurrent but distinctly different reactions taking place. In one case, the pseudohypochlorite acted as a source of chloronium ions, causing chlorination of the solvent and regenerating the original substituted phenol. In the other reaction, it appeared that an intermediate oxyphenonium ion may have been generated, which on reaction with the solvent produced a diphenyl ether derivative.

The Friedel-Crafts reaction of the pseudohypochlorite of tetrabromobiaphenol-A and benzene yielded a complex mixture of chlorine and bromine trisubstituted phenols.
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I. INTRODUCTION.

Only one reaction has been published in which an organic hypochlorite is reacted in the presence of a strong Lewis acid. Berman and Lowry (1) reacted tertiary butyl hypochlorite with benzene in the presence of aluminum chloride reporting tertiary butylbenzene as the product.

In view of Berman and Lowry's findings, it was felt that if aryl hypochlorites were substituted for the alkyl compounds, one conceivably might expect aryl ethers as one of the major products in the following manner:

\[
\begin{align*}
X-\text{Ph}-\text{O}-\text{alk} + \text{AlCl}_3 & \rightarrow [X-\text{Ph}-\text{O}]^+ \text{AlCl}_4^- \\
\text{Ph}_2\text{O}X & + \text{H}^+
\end{align*}
\]

If such a reaction were to take place, the reacting electrophile would be a species containing a positive oxygen which could be stabilized through resonance, an oxyphenonium ion.

In addition, it was felt that such a mechanism could result in the formation of polyethers if one were to use a substituted diphenolic compound instead of substituted
phenols. An attempt was made using tetrabromobisphenol A as the diphenolic compound.
II. HISTORICAL BACKGROUND.

Acyl hypohalites were first prepared in 1861 by Schultzenberger (2,3,4), who found that acetyl hypochlorite was formed by the action of chlorine monoxide on acetic acid. Although objections have been raised against this work, it has been confirmed spectrophotometrically(5). Since this time, many acyl hypohalites have been prepared(11).

Exhaustive studies of the properties of various acyl hypochlorites and hypobromites in solution have been made(6). Various kinetic investigations have been carried out in which acyl hypohalites have been proposed as intermediates. (11) Although no acyl hypohalite has been isolated from its corresponding solution, except as a complex, these substances are well-defined species in solution. A recent spectrophotometric study has shown the identity of acetyl hypohalites prepared by different methods (5).

Alkyl hypohalites were first obtained by Sandmeyer in 1885. Ethyl hypochlorite was the first ester of hypochlorous acid to be prepared (7). Sandmeyer's study of methyl and ethyl hypochlorites (8) was extended by Chattaway and Backeberg (9,10), who prepared other alkyl esters and studied their decomposition products. A good review of alkyl, as well as acyl, hypohalites was prepared by Anbar and Ginsberg (11).
The third group of esters of hypohalous acids consists of the aryl hypohalites. Of all of the reactions of hypohalous esters, those least documented are the phenolic esters. Deniville and Fort (12) prepared several compounds which they thought were aryl hypochlorites. They reported that the hypochlorites of unsubstituted phenols are extremely unstable and rearrange to ortho and para substituted phenols. Deniville and Fort were able to prepare and isolate several of these esters. They also report several methods of preparation and some physical data of these compounds - listed in Table I.

**Table I.** (12)

<table>
<thead>
<tr>
<th>Phenol</th>
<th>MP or BP of Hypochlorite</th>
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<tr>
<td>pentachlorophenol</td>
<td>51-52°C</td>
</tr>
<tr>
<td>3,5 dibromo-2,4,6-trichlorophenol</td>
<td>96-97°C</td>
</tr>
<tr>
<td>pentabromophenol</td>
<td>121-122°C</td>
</tr>
<tr>
<td>2,4,6-trichloro-3,5-xylenol</td>
<td>69-70°C</td>
</tr>
<tr>
<td>2,3,4,6-tetrachlorophenol</td>
<td>oil 116°C (1 mm)</td>
</tr>
<tr>
<td>2,4,6-trichloro-metacresol</td>
<td>oil, nondistillable</td>
</tr>
<tr>
<td>2,4,6-trichlorophenol</td>
<td>oil, BP 103°C (0.5 mm)</td>
</tr>
<tr>
<td>2,6 dichloro-para-tert-amy1-phenol α chloro-β naphthol</td>
<td>oil, nondistillable</td>
</tr>
</tbody>
</table>

The methods employed in the preparations of these compounds were:

1. The low temperature forced chlorination of the sodium salt of substituted phenols in an inert solvent such as carbon tetrachloride.
2. The low temperature reaction of aqueous hypo-
chlorous acid with the phenol in carbon tetrachloride.

3. The low temperature reaction of tertiary butyl
hypochlorite with the phenol in carbon tetrachloride.

These same authors (13,14,15) later found that the
hypochlorites prepared isomerized into their para quinoid
isomers, namely 1,4-cyclohexadiene -3- one structures in
which the oxy-chlorine moved to the 6 position. These
structures are mentioned to be thermodynamically more
stable by these authors (13), but they neglect to give
any reasoning for their greater stability.

King and McCollie (16), in 1913, reported that a
dichloride of a substituted phenol could be produced by
forced chlorination. They gave the structure of this
dichloride as a 1,4-cyclohexadiene -3- one.

The physical properties of the para quinoid structures
distinguish them from the hypochlorite isomers. The hypo-
chlorite isomers are yellow, low melting and soluble at
room temperature in the usual organic solvents. The
chlorocyclohexadiene-ones are colorless, higher melting
point, and hard to dissolve at room temperature in methanol
and acetic acid. However, the isomers behave similarly in
numerous chemical reactions. Thus they exhibit the same
chlorinating properties and they both lend themselves to quantitative analysis by iodine.

In the course of their work, Demville and Fort (16) found that the isomer which they had labeled as a hypo-chlorous ester was, in fact, the ortho quinoid isomer (i.e. 1,5-cyclohexadiene -3- one) with the oxy-chlorine going to the 4 position. These ortho quinoid isomers were yellow in color, low melting and in general exhibited the properties previously ascribed to the aryl hypochlorites. The preparation of aryl hypochlorites must then yield, not hypochlorites, but a mixture of ortho and para cyclohexadieneones as follows:

![Chemical Structures]

The authors gave ultraviolet and infrared data for these isomers - shown in Table II.

### Table II.

<table>
<thead>
<tr>
<th>Structure</th>
<th>Infrared ($\lambda_{\text{c}=0}$)</th>
<th>$\lambda_{\text{max}}$</th>
<th>$\varepsilon$</th>
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<tbody>
<tr>
<td>B</td>
<td>$5.38 \mu$</td>
<td>250-260 $\mu$</td>
<td>22,000</td>
</tr>
<tr>
<td>C</td>
<td>$5.83 \mu$</td>
<td>350-360 $\mu$</td>
<td>2100-3300</td>
</tr>
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III. EXPERIMENTAL.

Infrared spectra were obtained from a Baird Atomic Inc. Model 455 double beam infrared spectrophotometer with a rock salt prism permitting scans in the 2-16 micron range. All spectra were run as potassium bromide pellets unless otherwise indicated.

Ultraviolet spectra were run on a Perkin Elmer Model 202 Ultraviolet-and-Visible spectrophotometer. All samples were run using isooctane as the solvent.

Nuclear magnetic resonance spectra were run on a Varian A60 NMR spectrophotometer. Samples were dissolved in either carbon tetrachloride or deuterated chloroform.

Vapor phase chromatograms were run on a Beckman/G C-2 gas chromatograph employing a six foot Carbowax 1500 column, and a Bausch and Lomb 500 VOM 7 recorder. Helium was used as the carrier gas, at a constant temperature and pressure.

High temperature VPC work was conducted on a F and M 500 gas chromatograph using four foot SE 30 silicone rubber column and thermal conductivity detectors. Helium gas was used as the carrier and the heating rate was fifteen degrees per minute.

X-ray emission work was done on a General Electric XRD-3 X-ray Spectrophotometer. Chlorine emission work
employed the first order Kα line (2θ = 66°) using a flow detector, chromium target tube, sodium chloride crystal, and a 0.020 inch collimator. Bromine emission employed the first order Kα line (2θ = 29.96°) using a scintillation detector, platinum target tube, lithium chloride crystal and a 0.005 inch collimator.

Melting points were determined on a Fisher-Johns melting point apparatus with a heating rate of about 5 degrees per minute. The values used here were uncorrected by any standardization.

Column chromatographic work was done using a one inch diameter, eighteen inch long glass column with a column height of about eight inches. The packing used for all separations was Merck reagent grade aluminum oxide #61452.

A. PREPARATION OF THE PSEUDOHYPOCHLORITES* OF SUBSTITUTED PHENOLS.

1. Pseudohypochlorite of 2,4,6-trichlorophenol.

The pseudohypochlorite of 2,4,6-trichlorophenol, which is probably a mixture of 2,4,6,6-tetrachloro-1,4-cyclohexadiene-3-one and 2,4,4,6-tetrachloro-1,5-cyclohexadiene-3-one (17) was prepared by the forced chlorination

* Pseudohypochlorite is a term used for brevity.
of the sodium salt of 2,4,6-trichlorophenol in carbon tetrachloride according to a method given by Deniville and Fort (12).

Sodium 2,4,6-trichlorophenolate was prepared by first dissolving 4 g. (0.10 mole) of sodium hydroxide in 200-ml. of water, followed by a slow addition of 20 g. (0.101 mole) of 2,4,6-trichlorophenol, at room temperature. Stirring was continued until a solution was obtained. The resulting solution was filtered and then evaporated to dryness in an evaporating dish yielding 21.2 g. (0.096 mole) of product.

The pseudohypochlorite was prepared by first bubbling chlorine gas into 200-ml. of carbon tetrachloride at 50 °C (ice bath) until a saturated solution was obtained. A dispersion of 21.2 g. (0.097 mole) of sodium 2,4,6-trichlorophenolate in 50-ml. of carbon tetrachloride was added slowly. The chlorine was continually bubbled during the addition, and continued for about two additional hours.

The reaction product was then filtered to remove the sodium chloride formed, and the carbon tetrachloride was evaporated under vacuum, yielding 15 g. (66.6%) of a yellow oil. Infrared (Figure 4) and ultraviolet (Figure 25) spectra were determined.
2. **Pseudohypochlorite of Pentachlorophenol.**

The pseudohypochlorite of pentachlorophenol, which is probably a mixture of $1,2,4,5,6$-hexachloro-$1,4$-cyclohexadiene -3- one and $1,2,4,4',5,6$-hexachloro-$1,5$-cyclohexadiene -3- one (17), was prepared by a method given by Deniville and Fort (12).

The sodium salt of pentachlorophenol was prepared by the procedure described in section A.1 with a 90% yield. The hypochlorite was prepared by bubbling chlorine gas into $100$-ml. of carbon tetrachloride, maintained at $5^\circ$ C until a saturated solution was obtained. A cold dispersion of $39$ g. ($0.135$ mole) of sodium pentachlorophenolate in $100$-ml. of carbon tetrachloride was added slowly with stirring. A slight exotherm was noted, which caused the temperature to rise to $10^\circ$ C as the dispersion was added. Chlorine gas was bubbled in for an additional 30 min, after the addition of the sodium pentachlorophenolate. The resulting solution was then filtered to remove the sodium chloride formed. About $7$ g. ($0.12$ mole) of sodium chloride was collected. The solution was concentrated under vacuum at $50^\circ$ C. The remaining material was a yellow syrup which crystallized on cooling to bright yellow crystals, M.P. $50$-$53^\circ$ C, 31 g. (76.5%). The infrared spectrum of the pseudohypochlorite was obtained. (Figure 5) (M.P.lit. 51-52$^\circ$) (12)
3. Pseudohypochlorite of Tetrabromobisphenol-A.

The disodium salt and pseudohypochlorite were prepared by the procedure given in section A.1. A yield of 20 g. (66.8%) of a yellow semi-solid was obtained by reacting 28.3 g. (0.048 mole) of the sodium salt with chlorine. The infrared spectrum (Figure 6) was determined.

B. FRIEDEL-CRAFTS REACTIONS.

The Friedel-Crafts reactions were carried out on all of the pseudohypochlorites in either benzene or anisole which acted both as a reactant and solvent. In each case, aluminum chloride was used as the catalyst.

1. Pseudohypochlorite of 2,4,6-trichlorophenol in benzene.

Five grams (0.022 mole) of the pseudohypochlorite was dissolved in 40 g. of anhydrous benzene in a 250-ml. beaker. As the solution was stirred, 2.9 g. (0.022 mole) of aluminum chloride was added slowly. The stirring was continued until a negative starch-iodide test was noted, which took about 90 min. During this time, the reaction mixture temperature rose to 390 C and hydrogen chloride was evolved.

The reaction mixture was quenched in a 10% hydrochloric acid solution to convert the aluminum chloride into aluminum ion. The benzene layer was removed in a
separatory funnel and washed several times with a 10% sodium hydroxide solution. The sodium hydroxide layer was acidified with hydrochloric acid and the resulting solid filtered off. The solid material was 2,4,6-trichlorophenol (1.41 g, 0.007 mole).

The benzene layer was then distilled almost to dryness, and a vapor phase chromatograph of the resulting distillate was obtained. More benzene was added to the residue from the distillation and the resulting solution was put through an activated aluminum oxide column. The column was washed with a 70/30 ligroin/benzene solution. Yield from the column was 0.3 g. of a low melting solid, M.P. 43-60° C. The infrared spectrum of this solid was determined. (Figures 7 and 3)

The unknown compound(s) from the column was then recrystallized from isopropanol/water. The yield was about 10 milligrams of a material melting at 143° C. Its infrared (Figure 9) and ultraviolet (Figure 30) spectra were determined.

2. Pseudohypochlorite of 2,4,6-trichlorophenol with anisole.

A quantity of 3.6 g. (0.037 mole) of the pseudohypochlorite was dissolved in 70 g. of anhydrous anisole. An equal molar quantity (5.03 g.) of aluminum chloride
was added as the solution was stirred. A greater quantity of hydrogen chloride was evolved than in the benzene reaction (B.1). The reaction mixture was stirred until a negative starch-iodide test was noted.

The workup was identical with the benzene reaction (B.1). A vapor phase chromatogram was determined for the distilled anisole.

3. Pseudohypochlorite of Pentachlorophenol in benzene.

Nine grams (0.03 mole) of the pseudohypochlorite was dissolved in 70 g. of anhydrous benzene. An equal molar quantity (4.0 g.) of aluminum chloride was added slowly. The temperature of the mixture was maintained at 50-60° C. for 2 hr. during which time hydrogen chloride was evolved. The mixture was allowed to react until a negative starch-iodide test was obtained.

The mixture was treated exactly as before, except the residue from the distillation was treated with methanol. The methanol precipitated about 70 mg. of a solid material. This material was later redissolved in benzene and put through the aluminum oxide column to get rid of tars. The material from column was recrystallized from mixed isopropanol and water; M.P. 165-167° C.

The infrared (Figure 11), ultraviolet (Figure 31), and
nuclear magnetic resonance spectra were determined for this product.

4. Pseudohypochlorite of Tetrabromobisphenol-A in benzene.

A quantity of 19.7 g. (0.032 mole) of the hypochlorite of tetrabromobisphenol-A was dissolved in 80 g. of benzene. While the solution was stirred, an equal molar quantity (4.3 g.) of aluminum chloride was added. The reaction mixture was stirred for 2.5 hr. during which time hydrogen chloride was evolved. The reaction was continued until a negative starch-iodide test was observed. A gummy material precipitated out during the reaction, but was removed by the sodium hydroxide extraction. The benzene layer was distilled as before and a vapor phase chromatogram was obtained.

The sodium hydroxide layer was acidified with hydrochloric acid, and the resulting precipitate (about 10 g.) was dried. At this point, it was noticed that this material could be sublimed. Nuclear magnetic resonance (Figure 33), infrared (Figure 12) and ultraviolet (Figure 34) spectra were determined for the sublimed material. A high temperature vapor phase chromatogram (Figure 35) was made, which showed the sublimed material to be a complex mixture containing no less
than four major components. The four major components were trapped and their infrared spectra (Figures 15-18), and melting points were determined.

C. OTHER PREPARATIONS.

1. 2,6-Dichloro-4-methylphenol.

The method used to synthesize this product was that described by Zincke (13).

A quantity of 54 g. (0.5 mole) of p-cresol was dissolved in 270 g. of carbon tetrachloride. As the solution was stirred, chlorine gas was bubbled in for 2.5 hr. The temperature rose to 55° C so an ice bath was employed. After the chlorination, the mixture was steam distilled, and a low melting solid distilled over at 99° C. An infrared spectrum (Figure 20) was determined. No further work was tried on this product.

2. 2,4,6-Trichloroaniline.

A quantity of 20 g. (0.102 mole) of aniline was dissolved in 200-ml. of 10% hydrochloric acid. Chlorine gas was bubbled into the solution for 2 hr. A precipitate was formed which probably was the hydrochloride of the chlorinated aniline. A lot of tars were formed as a result of oxidation by chlorine. The infrared spectrum of the resulting compound indicated some 2,4,6-trichloroaniline present, but in poor yields.
A better preparation for this product is given by Orloff and Napolitano (19) but was not tried. All subsequent work using 2,4,6-trichloroaniline was carried out on material purchased from Eastman Chemicals Co.

3. 1-Iodo-2,4,6-trichlorobenzene.

The 1-iodo-2,4,6-trichlorobenzene was prepared by diazotizing 2,4,6-trichloroaniline and then converting the diazonium salt to the iodo compound by the Sandmeyer reaction as outlined by Willgerodt and Wilcke (20).

A quantity of 10 g. (0.051 mole) of 2,4,6-trichloroaniline was dissolved in 10-ml. of concentrated hydrochloric acid and 200-ml. of water in a 1000-ml. beaker, with constant stirring. The solution was then cooled to 5° C in an ice bath. A cold solution of 4 g. (0.058 mole) of sodium nitrite in 25-ml. water was added slowly with rapid stirring. During and subsequent to the addition of nitrite, the reaction mixture was kept below 5° C. About half of the 2,4,6-trichloroaniline failed to dissolve during the diazotization step and had to be filtered from the cold solution.

A quantity of 10 g. of potassium iodide in 100-ml. of water was added to the diazonium salt solution while stirring was maintained. When the addition of the potassium iodide was complete, the reaction mixture was
put on a steam bath and gently warmed until nitrogen evaporation ceased. The dark, tarry product precipitated, and was filtered.

The crude 1-iodo-2,4,6-trichlorobenzene was re-crystallized from alcohol, yielding 4 grams, M.P. 53-54° C. The infrared spectrum of this compound was determined (Figure 19). (M.P. lit. 54°) (20)

4. Phenyl diazonium fluoroborate.

Phenyl diazonium fluoroborate was prepared by a method identical to that given by Vogel (21) for the preparation of p-methoxy-phenyl diazonium fluoroborate. However, aniline was used instead of p-anisidine.

A quantity of 27.9 g. (0.3 mole) of aniline was dissolved in 190-ml. of 42 per cent fluoboric acid. This was diluted with an equal volume of water in a 600-ml. beaker. The solution was cooled to 5° C in an ice bath and stirred mechanically. A solution of 20.7 g. of sodium nitrite in 40-ml. of water was added slowly with the temperature maintained at 10° C. The solution was stirred vigorously towards the end of the reaction, and cooled below 5° C. The phenyl diazonium fluoroborate (light pink crystals) precipitated. The solution was then quickly filtered with a Buchner funnel and washed with 30-40-ml. of ice cold 5 per cent fluoboric acid and 40-ml.
of cold methanol. Suction was applied until the salt was dry. The product was removed from the filter and dried overnight. Phenylidiazonium fluoroborate is stable for several days at room temperature.

5. **Phenyl-2,4,6-trichlorophenyl Ether and Pentachlorophenyl-phenyl Ether.**

Attempts were made to prepare these ethers by the decomposition of phenylidiazonium fluoroborate in dimethyl sulfoxide (DMSO) in the presence of 2,4,6-trichlorophenol and pentachlorophenol.

Equal quantities (about 1 g.) of fluoborate and phenols were weighed out in separate beakers and dissolved in DMSO. Nitrogen evolution was immediately noted. The solutions were allowed to stand for several days at room temperature.

When the evolution of nitrogen ceased, each reaction mixture was poured into 100-ml. of water. A compound immediately precipitated in each case. The compounds were identified as 2,4,6-trichlorophenol and pentachlorophenol respectively. No ether formation was observed in either case.

6. **2-Chloro - 4,6-dibromophenol.**

The 2-chloro - 4,6-dibromophenol was prepared by a method given by Hunter and Joyce (22).
A quantity of 2.0 g. (0.016 mole) of o-chloro-phenol was dissolved in 50-ml. of glacial acetic acid in a 200-ml. Erlenmeyer flask. A stoichiometric amount of bromine (5.1 g., 0.032 mole) was added slowly while the solution was shaken, at room temperature. The reaction mixture was allowed to stand for several hours during which time hydrogen bromide was evolved.

About 100-ml. of water was then added to the solution and a white solid precipitated. The solid was filtered and washed several times with water. After drying, 2.1 g. of this material was recrystallized from a mixture of alcohol and water. Yield was 4.1 g. (89.5%) M.P. 74-75° C. An infrared spectrum (Figure 21) was determined for this compound. (M.P. lit. 76°) (22)

7. 4-Chloro - 2,6-dibromophenol.

This phenol was prepared in the same manner as 6.6.

A quantity of 2.0 g. (0.016 mole) of p-chloro-phenol was dissolved in 50-ml. of glacial acetic acid in a 200-ml. Erlenmeyer flask. A stoichiometric amount of bromine (5.1 g., 0.032 mole) was added slowly as the solution was shaken, at room temperature. The reaction mixture was allowed to stand for several hours during which time hydrogen bromide was evolved.

About 100-ml. of water was added to the solution
and a white solid precipitated. The solid was filtered and washed several times with water. After drying, the pure compound was recrystallized from a mixture of alcohol and water. Yield was 4.4 g. (96%) M.P. 90-92°C. An infrared spectrum (Figure 22) was determined for this compound. (M.P. lit. 92°C) (22)

8. 4-Bromo - 2,6-dichlorophenol.

The 4-bromo - 2,6-dichlorophenol was prepared by a method given by Hunter and Joyce (22).

A quantity of 2.0 g. (0.011 mole) of p-bromo-phenol was dissolved in 50-ml. of glacial acetic acid in a 200-ml. Erlenmeyer flask. Chlorine was bubbled in while the solution was shaken at room temperature. The reaction mixture was allowed to stand for several hours during which time hydrogen chloride was evolved.

About 100-ml. of water was then added to the solution and a yellow solid precipitated. The solid was filtered and washed several times with water. After drying, the pure material was recrystallized from a mixture of alcohol and water. Yield was 1.4 g. (26.2%) M.P. 66-68°C. An infrared spectrum (Figure 23) was determined for this compound. X-ray emission analysis of this compound showed essentially no bromine to be present. The infrared spectrum showed this compound to be 2,4,6-trichlorophenol.
9. Phenyl-2,4,6-trichlorophenyl Ether.

Another attempt was made at preparing this ether by the decomposition of a diazonium salt.

A quantity of 23-ml. (0.248 mole) of aniline was dissolved in 63-ml. of concentrated hydrochloric acid and 63-ml. of water in a 600-ml. beaker. The solution was then cooled to 50 ℃. A cold (5℃) solution of 18.25 g. (0.264 mole) of sodium nitrite in 50-ml. of water was added slowly. The temperature of the reacting solution was kept below 100 ℃ during the nitrite addition. The solution was tested periodically with starch-iodide paper until an immediate positive test was noted. This constituted an excess of nitrous acid and the addition of sodium nitrite was stopped. The diazonium salt solution was then maintained at 50 ℃ by the addition of a little ice.

About 100-ml. of the diazonium salt solution was withdrawn and made very slightly basic (pH 7-8) with a 5% solution of sodium bicarbonate with the temperature maintained at 50 ℃. An aqueous solution of about 1 g. of sodium 2,4,6-trichlorophenolate was then added and a precipitate was produced. The precipitate was then filtered. A test of the precipitate showed it to be insoluble in sodium bicarbonate.
About 0.3 g. of the damp precipitate was decomposed at 60-90° C. A water-insoluble gas (probably nitrogen) was evolved. Analysis of the products of the decomposition showed about 3.5-ml. of gas, 0.15 g. of water and 0.15 g. of a dark oily substance collected. The rest of the precipitate was then decomposed. No further work was done on this reaction at this time.

The remainder of the diazonium salt solution was treated with a solution of 38 g. (0.345 mole) of sodium fluoborate in 75-ml. of water. The temperature of the solutions were maintained below 10° C. After the addition of the sodium fluoborate, the resulting phenyl-diazonium fluoborate precipitated. The precipitated fluoborate salt was filtered with a Buchner funnel and quickly sucked dry. The partially dry salt was spread on filter paper and dried overnight. About 30 g. (0.157 mole) was collected. (Yield was 63.5%).

10. Phenyl-2,4,6-trichlorophenyl Ether.

Another attempt was made at preparing this ether by the decomposition of phenyl-diazonium fluoborate in the presence of sodium 2,4,6-trichlorophenolate in anisole.

A quantity of 9.46 g. (0.05 mole) of phenyl-diazonium fluoborate was suspended in 40 g. of anisole in a 100-ml. beaker. An equal molar quantity of 10.98 g. (0.05 mole) of sodium 2,4,6-trichlorophenolate was stirred into the
heterogeneous mixture.

As soon as the phenolate was added, nitrogen was observed. The nitrogen evolution was slow at first, and gradually increased; but never became very rapid. A slight exotherm caused the temperature to rise to about 31°C. A cooling bath was then employed to lower the temperature to 15-20°C. The heterogeneous mixture was allowed to react for several days.

The mixture was then filtered to remove the solids. The solids were washed several times with ether. The filtrate was then washed several times with sodium bicarbonate, to remove any 2,4,6-trichlorophenol present. The filtrate was then dried by washing with a saturated solution of sodium chloride in a separatory funnel. The ether-anisole layer was passed through a cone of anhydrous sodium sulfate. The ether was evaporated. Petroleum ether was then added to the anisole and about 1 g. of a solid material precipitated and was filtered. The filtrate was concentrated to about a 5 g. quantity in a Hickman vacuum still. This concentrated material was a sticky semi-solid.

Infrared and ultraviolet spectra were determined for the semi-solid as well as an infrared spectrum of the precipitated material. Further work on this reaction was continuing at the time of the writing of this thesis.
II. Pentachlorophenyl-phenyl Ether.

An attempt was made to prepare this ether by an identical method as mentioned before (C-10).

A quantity of 9.46 g. (0.05 mole) of phenyl diazonium fluoroborate was suspended in 25 g. of anisole in a 100-ml. beaker. An equal molar quantity of 14.4 g. (0.05 mole) of sodium pentachlorophenolate was stirred into the heterogeneous mixture. Nitrogen evolution was noted as being much slower than in the previous reaction using 2,4,6-trichlorophenolate. Little or no exotherm was noted. The mixture was allowed to react for several days.

The work-up of this reaction was identical with the previous reaction (C-10).

When the ether evaporated, a material which was soluble in base precipitated. Further work on this reaction was continuing at the time of the writing of this thesis.
IV. RESULTS AND DISCUSSION.

A. PSEUдоHYPOCHLORITES.

1. The pseudohypochlorite of 2,4,6-trichlorophenol.

Inspection of the infrared spectra of the pseudohypochlorite (Figure 4) showed a weak peak at 2.85 μ (3500 cm⁻¹). This peak was probably due to a phenolic hydroxyl stretching vibration, indicative of some phenolic impurity present in the pseudohypochlorite.

The pseudohypochlorite infrared spectrum also had a strong carbonyl stretching band at 5.30 μ (1725 cm⁻¹) indicating quinoid-like structure in accordance with Deniville, Fort and Farve (17). The 11.4 μ (899 cm⁻¹) peak associated with 1,2,3,5 aromatic tetra substitution (23) was missing from the pseudohypochlorite spectrum. The characteristic aromatic substitution peaks in the 5.0 to 6.0 μ region were masked by the carbonyl absorption and could not be used for identification purposes.

Normally, the 1,2,3,5 tetra substitution absorption appeared as a weak band at 5.30 μ (1725 cm⁻¹). The data above would substantiate a quinoid rather than an aromatic structure.

The ultraviolet spectrum of the pseudohypochlorite of 2,4,6-trichlorophenol had one large absorption, $\lambda_{\text{max}} = 348 \text{ μm}, \varepsilon = 2400$. (Figure 25)

From the infrared spectrum (Figure 4) and the ultraviolet spectrum (Figure 25), it appeared that the
ortho quinoid form of the pseudohypochlorite (i.e. 2,4,4,6-
tetrachloro-1,5-cyclohexadiene -3-one) was the predomi-
nant reaction product in accordance with the data and
conclusions drawn by Deniville and Fort (15) (17).

2. The pseudohypochlorite of pentachlorophenol.

Inspection of the infrared spectra of pentachloro-
phenol (Figure 2) and the resulting pseudohypochlorite
(Figure 5) revealed at once the reduction of the
hydroxyl stretching band at 2.95 μ. Comparison of the
rest of the two spectra showed that they were entirely
different compounds.

The equally intense strong peaks at 5.83 μ (1720 cm⁻¹)
and 5.90 μ (1698 cm⁻¹) were due to carbonyl stretching
vibrations in complete accord with Deniville, Fort, and
Farve for the ortho and para quinoid structures respective-
ly. (17) A comparison of the spectrum of the pseudohypo-
chlorite (Figure 5) with that of chloranil showed amazing
similarities with respect to major peaks. This suggested
some para quinoid contribution.

The possibility of some of the actual hypochlorite
being present should not be excluded. Close examination
of Figure 5 showed the presence of peaks of moderate
intensity at 3.06 μ (1240 cm⁻¹) and 13.64 μ (734 cm⁻¹)
indicating hypochlorite (O-Cl) bending and stretching
vibrations. This was in accord with conclusions which
Hedberg and Badger (24) drew on the spectrum of hypo-
chlorous acid.

The reaction product of the forced chlorination of
sodium pentachlorophenolate was very probably a mixture
of 1,2,4,5,6,6-hexachloro-1,4-cyclohexadiene -3- one, 1,2,4,4,5,6-hexachloro-1,5-cyclohexadiene -3- one, and
pentachlorophenyl hypochlorite.

3. The pseudohypochlorite of tetrabromobisphenol-A.

Inspection of the infrared spectrum of the pseudohypo-
chlorite (Figure 6) showed a large hydroxyl stretching
band at 2.37μ (3500 cm⁻¹) indicating a rather large
quantity of phenolic material remaining at the end of
the chlorination. A medium intensity carbonyl stretching
peak was noted at 5.78μ (1730 cm⁻¹) indicating that some
of the material was converted to the ortho quinoid form.
Peaks were observed at 8.06μ (1240 cm⁻¹) and 13.49μ
(741 cm⁻¹), indicating that some material probably
remained in the hypochlorite form and did not rearrange
to the quinoid forms.

The two quinoid as well as the hypochlorite structures
of tetrabromobisphenol-A were examined for steric hindrance
using Fisher-Hirschfelder models. The tetrahedral
carbon in the para position (i.e. the para quinoid structure)
showed the most hindrance. While the para quinoid was
the most hindered of the structures, it could not be ruled improbable based on the model tests.

**B. FRIEDEL-CRAFTS REACTIONS.**

As will be noted below, two concurrent types of reactions seem to occur with the Lewis acid used. The first, I, discussed is the behavior of the pseudohypo-chlorites as chlorinating agents for the solvent. The second reaction, 2., which seems to produce substituted diaryl ethers would do so, if indeed these are the products, by an intermediate oxyphenonium ion.

**1. Neutralization of the sodium hydroxide extract of the Friedel-Crafts reaction of benzene and the pseudohypo-chlorite of 2,4,6-trichlorophenol yielded among other things, a white solid which was identified by infrared comparison as 2,4,6-trichlorophenol. The neutralization of the sodium hydroxide extract of the Friedel-Crafts reaction of benzene and the pseudohypo-chlorite of pentachlorophenol yielded pentachlorophenol. A similar analysis of the neutralized extract of the reaction of anisole and the pseudohypo-chlorite of 2,4,6-trichlorophenol yielded 2,4,6-trichlorophenol. These identifications were made by comparison of their infrared spectra.**
The Friedel-Crafts reaction of the pseudohypochlorite of pentachlorophenol with benzene gave the highest yield of the regenerated phenol derivative. This was followed sequentially by the reaction of the pseudohypochlorite of 2,4,6-trichlorophenol with benzene and the pseudohypochlorite of 2,4,6-trichlorophenol with anisole.

At this point, it was not known whether the phenols were true products of reaction or the result of hydrolysis of unreacted pseudohypochlorites with sodium hydroxide. For this reason, the benzene and anisole solutions were distilled until almost all of the solvent was collected. The solvent could then be analyzed by vapor phase chromatography (VPC) for additional compounds, particularly chlorinated solvents.

Analysis of the benzene layer of the reaction of the pseudohypochlorite of 2,4,6-trichlorophenol showed chlorobenzene to be present in small amounts. The analysis consisted of comparing retention times of the suspected solution against a prepared solution containing known amounts of benzene and chlorobenzene, and by adding small amounts of chlorobenzene to the suspected solution and observing only peak enhancement of the chlorobenzene peak. The benzene solution had to be considerably concentrated to observe a significant chlorobenzene peak in the chromatogram. (Figure 26).
Similar analyses were conducted on the benzene solutions of the pseudohypochlorites of pentachlorophenol and tetrabromobisphenol-A. In each case, chlorobenzene was observed in the resulting chromatograms (Figures 27 and 28). The Friedel-Crafts reaction of the pseudohypochlorite of tetrabromobisphenol-A with benzene contained an extra peak in its VPC which was not identified. It was apparently a higher boiling material than chlorobenzene.

The benzene layer of the Friedel-Crafts reaction of the pseudohypochlorite of pentachlorophenol with benzene was partly distilled. The distillate contained about 2% chlorobenzene. This, of course, means that more chlorobenzene was probably left in the distilling flask since the distillation was not carried to dryness.

The anisole layer of the reaction of the pseudohypochlorite of 2,4,6-trichlorophenol with anisole was also analyzed by VPC and found to contain what appears to be three extra peaks. Figure 29 showed two of these peaks to lie at slightly longer retention times than the anisole peak, with the third peak coming some time still later. Undoubtedly, in relation to the chlorobenzene found before, at least one of the two closely adjacent peaks was probably a chlorinated anisole. However, no attempt was made to compare retention times of the two suspect peaks with chlorinated anisoles.
All of the distilled anisole and benzene layers were subjected to qualitative sodium fusion tests for the presence of halogen. All of the layers tested showed positive halogen tests, helping to substantiate the presence of chlorinated solvent found in the chromatograms. The reaction products of the pseudohypochlorite of pentachlorophenol showed the most halogen, helping to substantiate the VPC findings.

Since the reaction of the pseudohypochlorite of tetrabromobisphenol-A with benzene contained bromine, the sodium fusion test was run for chlorine and bromine. Several qualitative chemical tests failed to show any evidence for the presence of bromine. The residue from the sodium fusion was then analyzed by X-ray emission to detect the presence of bromine. The X-ray analysis showed no bromine to be present as a result of the sodium fusion tests. The halogen present, therefore, must necessarily be chlorine, helping to substantiate the presence of chlorobenzene found by VPC.

In partial summary, since a phenol and a chlorinated solvent were found as products of the reaction, one part of the Friedel-Crafts reactions could conceivably be as follows:
where ArH is benzene or anisole.

From the amounts of the products found, it may be said that the Friedel-Crafts reaction of the pseudohypochlorite of pentachlorophenol with benzene favored the formation of pentachlorophenol and the chlorinated solvent.

2. Aluminum chloride might conceivably have been expected to remove a chloride ion from the pseudohypochlorite, yielding a resonance stabilized oxyphenonium ion which could cause still another reaction to take place. The other reaction might well be as follows:
After the phenol resulting from the reactions was removed by the sodium hydroxide extraction and most of the solvent was distilled off for VPC analysis, the remaining material was redissolved in benzene, and the tars were removed by column chromatography. The eluted materials were then analyzed.

The infrared spectrum (Figure 7) of the eluted material from the benzene layer of the Friedel-Crafts reaction of the pseudohypochlorite of 2,4,6-trichlorophenol was determined. Analysis of this spectrum revealed several interesting points. First, a comparison with Figure 4 showed a definite disappearance of the carbonyl absorption associated with the quinoid structure of the pseudohypochlorite, and the reappearance of the absorption indicative of 1,2,3,5 aromatic substitution at 11.4 μ (877 cm⁻¹) (23).

Secondly, medium intensity benzene monosubstitution peaks were noted at 13.66 μ (748 cm⁻¹) and 14.33 μ (700 cm⁻¹). In addition, a more concentrated infrared spectrum was run and the 5.0 to 6.0 μ region was examined in more detail. (Figure 8). Examination of this spectrum in the 5.0 to 6.0 μ region showed what may be both monosubstitution and 1,2,3,5 tetra substitution to be present. This analysis, however, was not very definitive due to poor resolution in this area.
Dahlgard and Brewster (26) have determined the infrared and ultraviolet spectra for several highly substituted diaryl ethers. They found in general that:

(1) A substituent at a position ortho to the ether oxygen atom weakened the ether absorption band (1240 cm\(^{-1}\)) and split it into two closely adjacent bands. For example, they found that the ether peaks of 2-chlorophenyl-phenyl ether were at 1245 cm\(^{-1}\) and 1270 cm\(^{-1}\).

(2) A para substituent had little influence on the position or intensity of the ether band.

Figure 7 showed what may be ether peaks at either 8.16\(\mu\) (1225 cm\(^{-1}\)) or 8.00\(\mu\) (1250 cm\(^{-1}\)).

If the reaction product work-up by base extraction has replaced one chlorine ortho to the ether, absorption might occur. Normally, the chlorines were in a better position to cleave the ether band and lead to the present trichlorophenol. However, experiment showed that base treatment of the trichlorophenol, and even the pentachlorophenol, with some heating, and later regeneration of the phenol from the solid sodium salt led exclusively to the
original phenol with no replaced chlorines. Also, any replacement of chlorine by hydroxyl should have led to base solubility, which the "ethers" did not have.

An infrared spectrum (Figure 9) of the purified form of the same material given in Figures 7 and 8 was determined. It was noted that the original suspected phenyl-2,4,6-trichlorophenyl ether was low melting, (M.P. 43-60°C). The material left after several recrystallizations from isopropanol/water melted at 143°C. Inspection of Figure 9 showed first a loss of the suspected monosubstitution peak at 14.33 μ, and secondly a minor hydroxyl peak at 3.00 μ, which may well be moisture in the potassium bromide matrix. The suspected ether peak may be observed at either 3.17 μ (1225 cm⁻¹) or 3.00 μ (1250 cm⁻¹).

The only fundamental difference between Figures 7 and 9 was the absence of a suspected monosubstitution peak at 14.33 μ in Figure 9. Therefore, it could not, at this time, be ascertained whether the suspected monosubstitution peak at 14.33 μ was due to actual monosubstitution in the suspected ether or some benzenoid structure impurity.

The benzene layer of the Friedel-Crafts reaction of benzene and the pseudohypochlorite of pentachlorophenol was analyzed in the same manner as described before. The
infrared spectra of the resulting suspected ether (Figure 10 and 11) were determined.

Inspection of Figure 10 showed several interesting features. First was the disappearance of the carbonyl absorption (Figure 5) and chloranil-like structure associated with the quinoid forms of the pseudohypochlorite. Second was the appearance of aromatic C-H stretching vibrations at 3.33 μ (3000 cm⁻¹). Since the penta-chlorophenol used to begin this reaction sequence had no aromatic C-H, this resulting vibrational frequency must necessarily have come from a reacted molecule of benzene. Further substantiating evidence came from the appearance of monosubstitution peaks at 13.42 μ (744 cm⁻¹) and 14.33 μ (700 cm⁻¹). What appeared to be a penta substitution peak was noted at 5.80 μ (1725 cm⁻¹) in accordance with Young, DuVall and Wright (25). The suspected ether peaks were observed at either 3.23 μ (1213 cm⁻¹) or 7.36 μ (1272 cm⁻¹) in accordance with Dahlgard and Brewster (26).

After the suspected pentachlorophenyl phenyl ether was recrystallized several times from isopropanol/water, a compound melting at 165°C was obtained, and its infrared spectrum (Figure 11) was determined. The first thing that was observed from this spectrum was the apparent loss of the monosubstitution peaks at 14.33 μ. However,
aromatic C-H stretching vibrations can be observed at 3.45 \( \mu \) (2900 cm\(^{-1}\)) indicating the presence of some aromatic hydrogen. Suspected ether peaks were still present at either 8.26 \( \mu \) or 7.88 \( \mu \).

Again, the only major difference between Figures 10 and 11 is the suspected monosubstitution peak at 14.33 \( \mu \) in Figure 10. It could not be ascertained whether this peak is due to monosubstituted benzene in the suspected ether or some benzenoid structure impurity (e.g. chlorobenzene).

A nuclear magnetic resonance (NMR) spectrum was determined for the suspected pentachlorophenyl phenyl ether. A poor spectrum was obtained due to the low concentration of the compound in deuterated chloroform. Only aromatic hydrogen (\( \delta = 7.54 \) ppm) was noted however, and the spectrum was indicative of non-equivalent hydrogens. Because of the poor spectrum, further analysis was impossible.

A quantity of 2.1 mg. of this material was analyzed for carbon and hydrogen. The sample size was insufficient for a chlorine analysis. Analysis by Drs. Weiler and Strauss (Oxford University) showed 48.55% carbon and 1.94% hydrogen to be present. Calculated carbon and hydrogen percentages for pentachlorophenyl-phenyl ether are 42.2 and 1.46% respectively.
Since there was no chlorine analysis, and since on this small a sample, the hydrogen analysis had great potential error, the ratio of carbon to hydrogen was not trustworthy. One could only say that the carbon analysis did not fit for di-ether formation with benzene, for the extra chlorine would then make for less carbon content. Neither could the replacement of chlorine be postulated, for then the spectral data would be in conflict (without hydroxyl on the infrared or hydroxyl hydrogen on the NMR). Solubility data would also be in conflict, particularly the lack of base solubility.

Ultraviolet spectra were obtained for the purified compounds from the Friedel-Crafts reactions of the pseudo-hypochlorites of 2,4,6-trichlorophenol and pentachlorophenol and benzene. (Figures 30 and 31 respectively) Comparison of Figures 30 and 31 with spectra of phenyl ether and bis-2-chlorophenyl ether (Figure 32) obtained by Dahlgard and Brewster (26) showed similarities in the region of 240 to 360 μμ. Further comparison of the four spectra showed what might be a bathochromic shift due to increased chlorine substitution on the benzene rings. A similar shift was observed in the ultraviolet spectra of 2,4,6-trichlorophenol and pentachlorophenol (Figure 36).
In summary of the discussion to this point, it appears that at least two concurrent but distinctly different reactions occurred when the aryl pseudohypochlorites were treated with aluminum chloride in the presence of benzene. In one case, the pseudohypochlorite acted as a source of chloronium ions, causing chlorination of benzene, and leaving a complex which on hydrolysis regenerated the original chlorinated phenol. In the other reaction, it appeared that an intermediate oxyphenonium ion may have been generated, which, on reaction with benzene, produced a diaryl ether derivative. The relation of relative amounts of solvent chlorination to diaryl ether formation seemed to range from ratios of 1.5 to perhaps over 100, with total yields of 50% to 90% estimated.

It should be noted that the Friedel-Crafts reactions of the pseudohypochlorites of 2,4,6-trichlorophenol and pentachlorophenol were run at 30° and 60° respectively. The reaction involving the pseudohypochlorite of pentachlorophenol needed heat to initiate its reaction.

It should also be noted at this point that attempts to synthesize phenyl-2,4,6-trichlorophenyl ether and pentachlorophenyl-phenyl-ether for spectral comparison with the suspected ethers have not been successful. Further work was continuing at the time of writing this thesis.
The evidence for proposing these compounds as products of the Friedel-Crafts reactions was based mainly on the infrared data; and specifically, on the presence of the aromatic C-O band at about 3.0 \mu\text{m}, and the close comparison of the ultraviolet data with the data of Dahlgard and Brewster.

The Friedel-Crafts reaction of the pseudohypochlorite of tetrabromobisphenol-A and benzene gave a rather large amount of material which was soluble in the sodium hydroxide extraction. Analysis of the benzene layer gave little, if any, product.

After it was known that the regenerated phenol products from the hydroxide extraction layer could be sublimed, about 3 g. of the material was sublimed for analysis. A nuclear magnetic resonance spectrum was determined for the sublimed material (Figure 33). The NMR spectrum showed the following:

(1) Aromatic (\( \delta = 7.40 \) ppm) and hydroxyl (\( \delta = 5.69 \) ppm) hydrogens with a small amount of possible aliphatic hydrogen (\( \delta = 2.22 \) and 2.31 ppm).

(2) A set of complex aromatic hydrogen peaks indicating non-equivalent hydrogens.
(3) Integration of the peaks showed 2 aromatic hydrogens to 1 hydroxyl hydrogen.

(4) The coupling constant for the aromatic hydrogens ($J_{AB} = 3.2$ cps) was indicative of different hydrogens meta to each other.

(5) Lack of symmetry and the complexity of the aromatic hydrogen peaks indicated that this might be a mixture.

The infrared spectrum (Figure 12) of the sublimed materials was determined. Analysis of this spectrum showed a definite hydroxyl stretching frequency at $3.00 \mu$ (3270 cm.$^{-1}$). The peak at $5.78 \mu$ (1731 cm.$^{-1}$) was indicative of 1,2,3,5 tetra substitution (25). (Compare with spectrum of 2,4,6-trichlorophenol, Figure 1).

Figure 14 showed the 5.0 to 6.0 $\mu$ region of the same material in a concentrated hexachlorobutadiene mull. An aliphatic C-H stretching band could be seen at $3.45 \mu$ (2900 cm.$^{-1}$). The band(s) at $5.78 \mu$ (1731 cm.$^{-1}$) are indicative of 1,2,3,5 tetra substitution. In general, the infrared spectrum of the sublimed material was indicative of a 2,4,6-trisubstituted phenol.

The ultraviolet spectrum (Figure 34) of the sublimed material was determined. Extinction coefficients and absorption wave lengths were determined for the principal peaks (Table III).
TABLE III

Concentration: \( 1 \times 10^{-4} \) M in Isooctane.

<table>
<thead>
<tr>
<th>( \lambda_{\text{max}} )</th>
<th>( \epsilon )</th>
</tr>
</thead>
<tbody>
<tr>
<td>214</td>
<td>14,500</td>
</tr>
<tr>
<td>288</td>
<td>2,600</td>
</tr>
<tr>
<td>298</td>
<td>2,600</td>
</tr>
</tbody>
</table>

Comparison of this spectrum with the ultraviolet spectra (Figure 36) obtained for 2,4,6-trichlorophenol and pentachlorophenol showed good agreement.

The solubility behavior of the sublimed material (Table IV) showed it to be a class \( A_1 \) substance and again indicated a negatively substituted phenol.

TABLE IV

<table>
<thead>
<tr>
<th>H(_2)O</th>
<th>NaOH</th>
<th>NaHCO(_3)</th>
<th>Class</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>( A_1 )</td>
</tr>
</tbody>
</table>

Analysis by X-ray emission showed the material to contain 30.3% Br and 9.2% Cl.

Since no combination of chlorine and bromine in a trisubstituted phenol fitted the X-ray analysis and because of an unusual NMR spectrum, a mixture was suspected. The sublimed material was put through a high temperature vapor phase chromatograph. The chromatogram (Figure 35) of this material showed it to be a complex mixture containing at least four major components. Approximate percentages of the four major peaks were determined. (Table V)
TABLE V.

<table>
<thead>
<tr>
<th>Peak</th>
<th>% of Total</th>
<th>Melting Point</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>21.8</td>
<td>54 - 62°C</td>
</tr>
<tr>
<td>2</td>
<td>43.6</td>
<td>60 - 65°C</td>
</tr>
<tr>
<td>3</td>
<td>27.2</td>
<td>66 - 72°C</td>
</tr>
<tr>
<td>4</td>
<td>7.4</td>
<td>83 - 86°C</td>
</tr>
</tbody>
</table>

The compounds associated with each of the VPC peaks were trapped and their melting points (Table V) and infrared spectra were determined. (Figures 15 through 18). Analysis of the infrared spectra showed all of the compounds to contain hydroxyl (3.00 μ) and 1,2,3,5 tetra substitution (11.4 μ and 5.0 - 6.0 μ region), indicative of trisubstituted phenols.

Analysis of the trapped compounds by X-ray emission showed the following:

<table>
<thead>
<tr>
<th>Compound</th>
<th>Chlorine</th>
<th>Bromine</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>2</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>3</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>4</td>
<td>No</td>
<td>Yes</td>
</tr>
</tbody>
</table>

Compounds 1 and 4 were immediately suspected as being 2,4,6-trichloro and 2,4,6-tribromophenol respectively. Comparison of their infrared spectra with the spectra of chloro and bromo trisubstituted phenols showed a conclusive match for both.
Since the X-ray analysis showed chlorine and bromine to be present in compounds 2 and 3, it was decided that these compounds would be found in the four possible arrangements involving chlorine and bromine in a trisubstituted phenol. Comparison of compound 3 (Figure 17) with the infrared spectrum of 2-chloro-4,6-dibromophenol (Figure 21) showed a good comparison with respect to major peaks. The differences in the two spectra appeared as minor peaks or shoulders in the spectrum of compound 3. These differences could conceivably be due to impurities as shown in the non-sharp melting point of compound 3 (Table V).

From the complex aromatic NMR spectrum (indicating non-equivalent hydrogens), the solubility data, infrared spectrum, and the fact that both chlorine and bromine were present, compound 2 could conceivably be 2-bromo-4,6-dichlorophenol. At the present time, 2-bromo-4,6-dichlorophenol has not been synthesized for comparison with compound 2.

From comparison of infrared data, the following structures were assigned to the four major VPC peaks:

<table>
<thead>
<tr>
<th>Compound</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2,4,6-trichlorophenol</td>
</tr>
<tr>
<td>2</td>
<td>(2-bromo-4,6-dichlorophenol)</td>
</tr>
<tr>
<td>3</td>
<td>2-chloro-4,6-dibromophenol</td>
</tr>
<tr>
<td>4</td>
<td>2,4,6-tribromophenol</td>
</tr>
</tbody>
</table>
An interesting result was obtained when the pseudohypochlorite of tetrabromobisphenol-A was heated. When heating the pseudohypochlorite, a material was sublimed off along with a gas which was acid to litmus. (Whether this gas was hydrogen chloride or hydrogen bromide was not known — although a hydrogen chloride odor was noticeable.) The infrared spectrum (Figure 13) of this material was obtained. Comparison of this spectrum with the spectrum of the mixed phenols (Figure 12) showed a good comparison.

From all the previous data concerning the products of the Friedel-Crafts reaction of the pseudohypochlorite of tetrabromobisphenol-A, it was felt that the chlorination of the sodium salt of tetrabromobisphenol-A caused a partial displacement of the bromine with chlorine. A similar situation was noted by Deniville and Fort (15) in the chlorination of bromo-substituted phenols.

At this point, it was not known whether the cleavage of the tetrabromobisphenol-A molecule or the resulting pseudohypochlorite was due entirely to the chlorination of the sodium salt or to the Friedel-Crafts catalyst. At any rate, the final result was a complex mixture of products.

The presence of aliphatic groups in the sublimed material from the Friedel-Crafts reaction could be due to the isopropyl group in the tetrabromobisphenol-A structure.
Since the presence of aliphatic hydrogen in the NMR spectrum (Figure 33) was slight and since the VPC failed to isolate a compound containing aliphatic groups, such a compound could be present in relatively small amounts in the volatile components.

C. OTHER PREPARATIONS.

When the crude reaction product of the chlorination of p-bromophenol was analyzed by X-ray emission, little, if any, bromine was detected. The infrared spectrum of the crude material showed what might be a weak carbonyl absorption at $5.77\mu$ (1730 cm$^{-1}$) indicative of the presence of some probable quinone structure. Sublimation of the crude material yielded a compound whose infrared spectrum gave a close comparison to 2,4,6-trichlorophenol with respect to major peaks.

Apparently, bromine was replaced by chlorine during the chlorination of the phenol in glacial acetic acid. King and McCombie (16) reported a similar situation in the chlorination of 2,4,6-triodophenol in glacial acetic acid.

The attempt to prepare phenyl-2,4,6-trichlorophenyl ether and pentachlorophenyl-phenyl ether by the decomposition of phenyl diazonium fluoborate in dimethyl sulfoxide (DMSO) gave 2,4,6-trichlorophenol and pentachlorophenol.
as the products instead of the ethers. The proposed reaction was to have been as follows:

\[
\text{DMSO} \quad \text{N}_2^+ \text{BF}_4^- + \text{Ph} - \text{OH} \xrightarrow{\text{DMSO}} \]

\[
\text{Ph} - \text{O}^- - \text{Ph} + \text{N}_2
\]

Since DMSO was in great excess as opposed to the phenols, what actually took place was probably:

\[
\text{N}_2^+ \text{BF}_4^- + \text{CH}_3 - \text{S} - \text{CH}_3 \xrightarrow{\text{DMSO}} \]

\[
\text{CH}_3 - \text{S} - \text{CH}_3, \text{BF}_4^- + \text{N}_2
\]

with no reaction with the substituted phenol taking place.
In another attempt to prepare phenyl-2,4,6-trichlorophenyl-ether, a slightly basic solution of phenyl-diazenium chloride was treated with a solution of sodium 2,4,6-trichlorophenolate. A precipitate was immediately formed and collected.

Thermal decomposition showed a non water-soluble gas to be evolved, which was collected and measured. If the gas was nitrogen, then the material might conceivably be phenyl-diazenium 2,4,6-trichlorophenolate. The thermal decomposition of this salt should have yielded phenyl-2,4,6-trichlorophenyl ether. A complete analysis of this reaction had not been carried out at the time of writing.

A third attempt at preparing phenyl-2,4,6-trichlorophenyl ether was tried. This time phenyl-diazenium fluoborate was reacted with sodium 2,4,6-trichlorophenolate in anisole. A solid and a semi-solid material were isolated as products.

A comparison of the infrared and ultraviolet spectra of the crude semi-solid and the infrared spectrum of the crude solid with Figures 7 and 30 showed slight comparisons. No positive identification could be made at this time and work was continuing at the time of writing.
V. SUMMARY AND CONCLUSIONS.

(1) The forced chlorination of the sodium salt of a substituted phenol in an inert solvent yielded 1,4-cyclohexadiene-3-one and 1,5-cyclohexadiene-3-one, and perhaps some phenylhypochlorite.

(2) The Friedel-Crafts reaction of the aryl pseudohypochlorites with benzene involved at least two concurrent but distinctly different reactions. In one case, the pseudohypochlorite acted as a source of chloronium ions, causing chlorination of benzene, and leaving a complex, which on hydrolysis regenerated the original chlorinated phenol. The Friedel-Crafts reaction of the pseudohypochlorite of pentachlorophenol appeared to favor this route.

In the other reaction, it appeared that an intermediate oxyphenonium ion may have been generated, which on reaction with benzene produced a diaryl ether derivative. Although all the evidence was not conclusive, the combination of infrared and ultraviolet spectra and the close correlation of these spectra with the spectra of the diaryl ethers prepared by Dahlgard and Brewster showed such formation to be very likely.

(3) The Friedel-Crafts reactions of the pseudo-
hypochlorite of tetrabromobiophenol-A with benzene gave
in addition to the chlorinated solvent, a complex mixture of trisubstituted phenols indicating at least the replacement of some of the bromine atoms with chlorine, along with cleavage of the tetrabromobisphenol-A molecule.
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Infrared spectrum of 2,4,6-trichlorophenol

**FIGURE 1**

Infrared spectrum of pentachlorophenol

**FIGURE 2**
Infrared spectrum of the pseudohypochlorite of pentachlorophenol

**Figure 5**

Infrared spectrum of the pseudohypochlorite of tetrabromobisphenol-A

**Figure 6**
Infrared spectrum of suspected phenyl-2,4,6-trichlorophenyl ether
(purified from column)

FIGURE 7

Infrared spectrum of suspected phenyl-2,4,6-trichlorophenyl ether
(more concentrated)

FIGURE 8
Infrared spectrum of suspected pentachlorophenyl-phenyl ether (recrystallized)

Infrared spectrum of the sublimed products from the Friedel-Crafts reaction of the pseudohypochlorite of tetrabromobisphenol-A and benzene
Infrared spectrum of the sublimed material resulting from the heating of pseudohypochlorite of tetrabromobisphenol-A

**Figure 13**

Infrared spectrum of the sublimed products from the Friedel-Crafts reaction of the pseudohypochlorite of tetrabromobisphenol-A and benzene-hexachlorobutadiene mull

**Figure 14**
Infrared spectrum of first VPC fraction of the Friedel-Crafts reaction of the pseudohypochlorite of tetrabromobisphenol-A (with benzene)

Infrared spectrum of the second VPC fraction
Infrared spectrum of the third VPC fraction

FIGURE 17

Infrared spectrum of the fourth VPC fraction

FIGURE 18
Infrared spectrum of 4-bromo-2,6-dichlorophenol

**Figure 23**

Infrared spectrum of phenyl ether

**Figure 24**
Figure 25
Ultraviolet spectrum of the pseudohypochlorite of 2,4,6 trichlorophenol. Solvent isooctane.

Absorbance

250 Wavelength 300 nm

200

0.01

0.1

0.2

0.3

0.4

0.5

0.6

0.7

0.8

0.9

1.0

1.1

1.2

1.3

1.4

1.5

4 x 10^{-5} M
FIGURE 26

--- concentrated original solution
----- added chlorobenzene

VPC of concentrated benzene layer of the Friedel-Crafts reaction of the pseudohypochlorite of 2,4,6-trichlorophenol and benzene. Column temperature 190° C.

FIGURE 27

--- concentrated original solution
----- added chlorobenzene

VPC of concentrated benzene layer of the Friedel-Crafts reaction of the pseudohypochlorite of pentachlorophenol and benzene. Column temperature 190° C.
FIGURE 28

VPC of concentrated benzene layer of the Friedel-Crafts reaction of the pseudohypochlorite of tetrabromobisphenol-A and benzene. Column temp. 190°C

---

FIGURE 29

VPC of concentrated anisole layer of the Friedel-Crafts reaction of the pseudohypochlorite of 2,4,6-trichlorophenol. Column temperature 190°C.
FIGURE 30

Ultraviolet spectrum of suspected phenyl-2,4,6-trichlorophenyl ether in isooctane
FIGURE 31
Ultraviolet spectrum of suspected pentachlorophenyl-phenyl ether in isooctane.
FIGURE 32

Ultraviolet spectrum of bis-2-chlorophenyl ether and phenyl ether from Dahlgard & Brewster (26).
FIGURE 33

Enlarged aromatic region

NMR of sublimed reaction products of the Friedel-Crafts reaction of the pseudohypochlorite of tetrabromobisphenol-A and benzene.
(Solvent CCl₄)
FIGURE 34

Ultraviolet spectrum of the sublimed reaction products of the Friedel-Crafts reaction of the pseudohypochlorite of tetrabromobisphenol-A and benzene. Concentration: $10^{-4}$ molar in isooctane.
VPC of the sublimed reaction products of the Friedel-Crafts reaction of the pseudohypochlorite of tetrabromo-bisphenol-A and benzene.
Figure 36

Ultraviolet spectra of 2,4,6-trichlorophenol and pentachlorophenol in isooctane.