STUDIES OF ARYL HYPOCHLORITES

by

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TABLE OF CONTENTS

INDEX OF ILLUSTRATIONS AND GRAPHS

Of all the reactions of the esters of hypohalous acids, those least documented are the reactions and characteristics of the phenolic esters. This includes the reactions of hypohalites in the presence of a strong Lewis acid, such as aluminum trichloride.

The preparation of several hypochlorous acid esters based on substituted phenols has been reported by Deniville and Fort (2). They reported several methods of preparation and some physical data on the hypochlorites prepared.

Subsequently, Deniville and Fort noted that the hypochlorites prepared isomerized to a 1,4-cyclohexadien-3-one structure with the hypochlorite chlorine moving to the 6 position (3). This rearrangement is catalysed by iodine, metal chlorides or hydrohalogen acids. The isomers show marked differences in solubility and physical characteristics from the hypochlorites.

These cyclohexadienone structural isomers have characteristic absorbtion bands in the ultraviolet in the region 260-290 millimicrons, the exact wavelength dependent on the type of substitution (5).

Aryl hypochlorites have the same properties as the alkyl esters of hypochlorous acid, i.e., they are chlorinating agents and oxidizing agents. In the 1,4-cyclohexadien-3-one structure, these properties are retained. However, Deniville and Fort have reported that pentachlorophenyl hypochlorite isomerizes to 1,2,4,4,5,6-hexachloro-1,5-cyclohexadien-3-one and undergoes a Diels-Alder condensation with maleic anhydride (4).

Only one reaction has been published in which an organic hypohalite is reacted in the presence of a strong Lewis acid; this dealt with an alkyl hypochlorite. Berman and Lowy (1) reacted tertiary butyl hypochlorite with benzene in the presence of aluminum trichloride, reporting tertiary butylbenzene as the product.

EXPERIMENTAL

A. Tertiary butyl hypochlorite was prepared as follows. Chlorine gas was bubbled into 230 ml. of water containing 11.5 g of calcium carbonate in suspension and 17.0 g of tertiary butyl alcohol. The temperature was maintained at 0-11° and chlorine was added, with gentle stirring, until all the calcium carbonate had dissolved (6). The upper layer of tertiary butyl hypochlorite was removed with a transfer pipette and stored over anhydrous magnesium sulfate, in a brown glass bottle.

B. 2,4,6-trichlorophynyl hypochlorite was prepared by reacting 0.05 mole (9.88 g) of 2,4,6-trichlorophenol with 0.055 mile (6.0)g) of tert.-butyl hypochlorite in 15 cc. of carbon tetrachloride. The mixture was heated to 40° and stirred until the solution became clear (2). The solution was concentrated under reduced pressure but the product was not isolated.

C. 5.80 g of the above crude 2,4,6-trichlorophenyl hypochlorite in benzene were added dropwise to a benzene-aluminum trichloride complex in nitrobenzene, with the temperature kept low. After addition of the hypochlorite, the mixture was allowed to reach room temperature and then stirred for two hours.

One hundred milliliters of distilled water were added slowly, in two fifty ml. portions. The layers were separated and the organic layer retained for analysis.

A portion of the organic layer was concentrated under reduced pressure and separated by thin-layer chromatography. The substrate used was aluminum oxide-G and the solvent was acetone. Each plate was developed three times for twenty minutes each time.

Three plates were chosen for further analysis. Fraction AA-1 (see figure 1) moved with the solvent front, AA-2 and AA-3 were intermediate fractions and AA-Base was the material remaining at the baseline. The material removed from each section was placed in a fifty ml. Erlenmeyer flask, covered with 25 ml. of 2,2,4-trimethylpentane, stoppered, and left for 24 hours at room temperature.

The four solutions were filtered. The ultraviolet spectra of these solutions, with 2,2,4-trimethylpentane as a blank, were measured on a Beckman DU spectrometer over the interval 215-330 millimicrons (figures 2-5).

Each of the four solutions showed oxidative properties upon testing with starch-iodide paper.

DISCUSSION

The analysis of the Friedel-Crafts reaction is far from complete. The initial thin-layer chromatography gave at best a partial separation as is indicated by the facts that all four solutions showed oxidative properties and that the three similar ultraviolet spectra from sections AA-2, AA-3 and AA-Base (figures 3-5) have their plateaus at the same wavelengths as the absorption peaks in the ultraviolet spectrum of AA-1.

Diphenyl ether has absorption peaks in the region 220-230 millimicrons and 270-280 millimicrons (7,8) with the 220-230 region showing the stronger absorption, as in the case of sample AA-1. Thus it is possible that sample AA-1 actually contains the desired ether, possibly mixed with some 2,4,6,6-tetrachloro-1,4-cyclohexadien-3-one. The cyclohexadien-3-one absorbs in the region 250-260 millimicrons (5). This would account for the peak at 255 millimicrons.

The strong absorption of sample AA-1 is evident from the fact that the graph is for a 1:5 dilution of the original solution. The 220-230 millimicron region, however, is not resolved until the original solution has been diluted 1:25.

The shifting of the second peak is probably due to the substitution of chlorine on only one benzene ring in the molecule.

Thus, the postulation that AA-1 is the product actually desired, 2,4,6-trichloro-1-phenoxybenzene, is a better conclusion than the postulation that AA-1 is 2,4,6,6-tetrachloro-1,4-cyclohexadien-3-one. The reference data for the isomerized hypochlorite make no mention of the 225-7 and 285-290 millimicron peaks, yet these are the strongest absorptions. Although the 255 millimicron peak is stronger than the 285-290 millimicron peak, this, more likely, is the result of being a shoulder on the very strong 225-7 millimicron peak.

If AA-1 is actually the diaryl ether, several interesting points become evident. One is the possibility that, during the reaction, the oxygen carries a positive charge. Second is that the O-Cl dissociation which, in the alkyl compounds, cleaves by a free radical mechanism has occurred through an ionic mechanism. On these possibilities alone, the idea merits further study, if only to the point of proving the structures of the products.

If,on the other hand, the diaryl ether was not produced, the subject still merits further attention, solely for the purpose of studying the kinetics of the isomerism and determining the mechanism by which it occurs. It is possible and probable that aluminum trichloride catalyzes the rearrangement from the hypochlorite to the cyclohexadienone (3). Since there is no published data on the effect of a strong Lewis acid on the rearrangement, a comprehensive study would be in order.

In the event that sample AA-1 might be nitrobenzene the spectrum was checked against that of nitrobenzene and the conclusion reached that AA-1 could not possibly be nitrobenzene.

BIOGRAPHY

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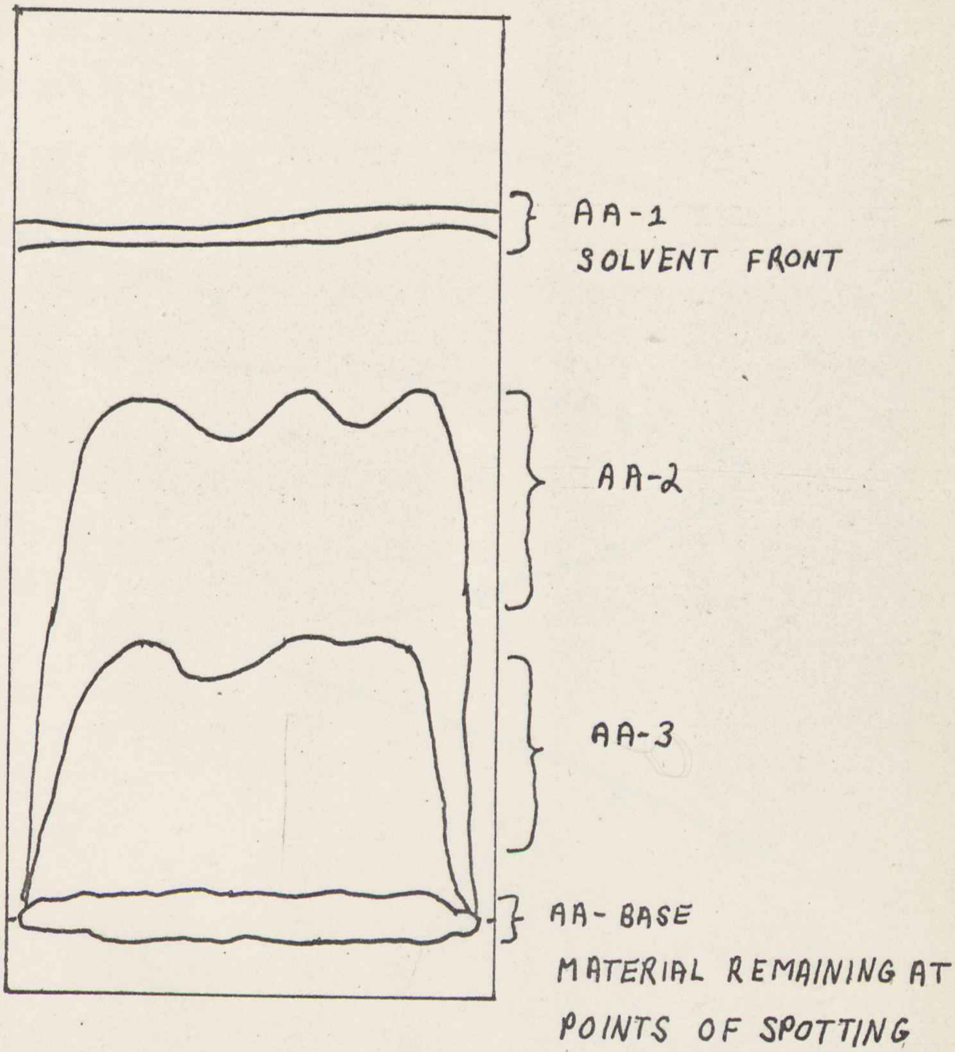
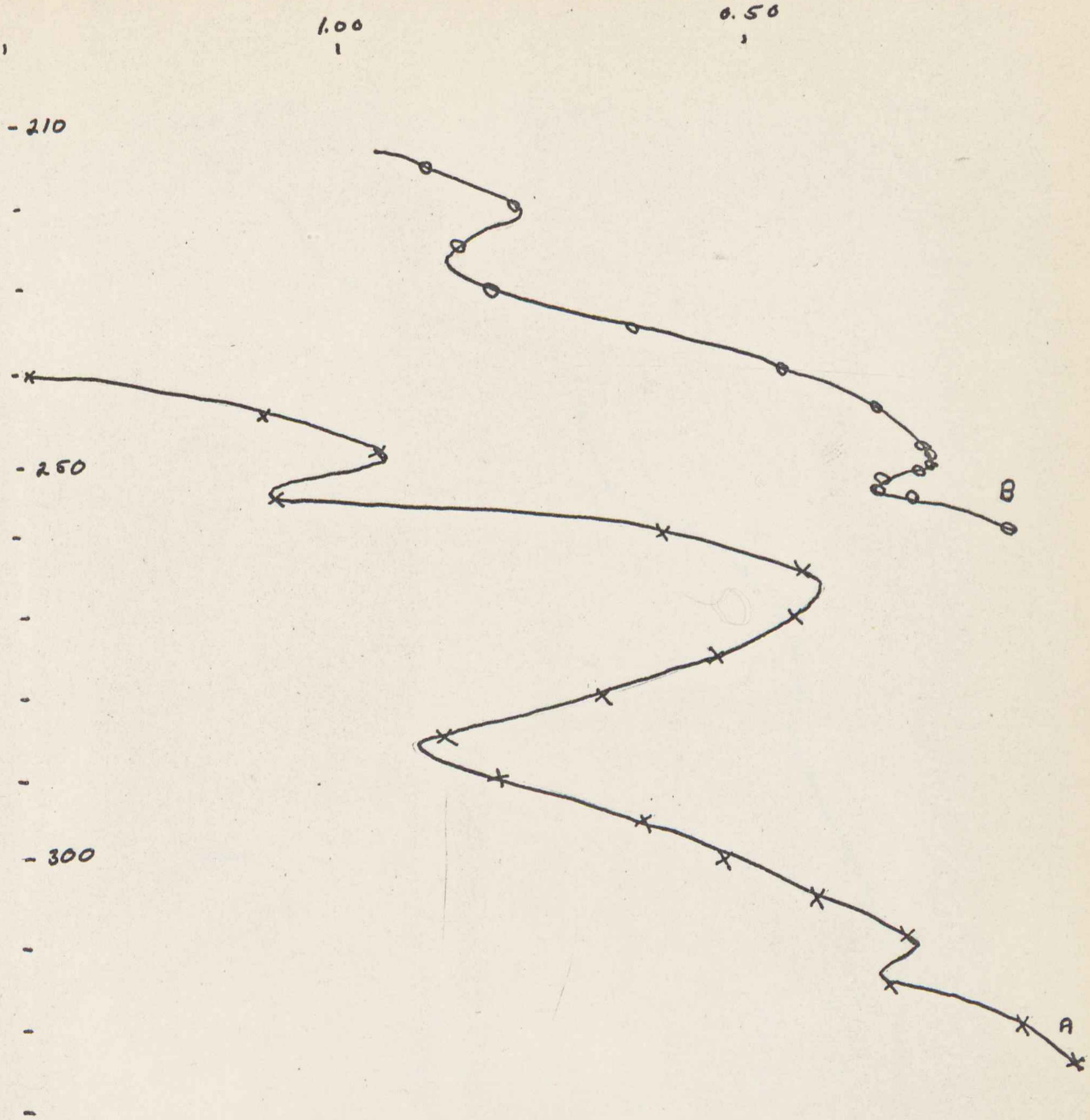


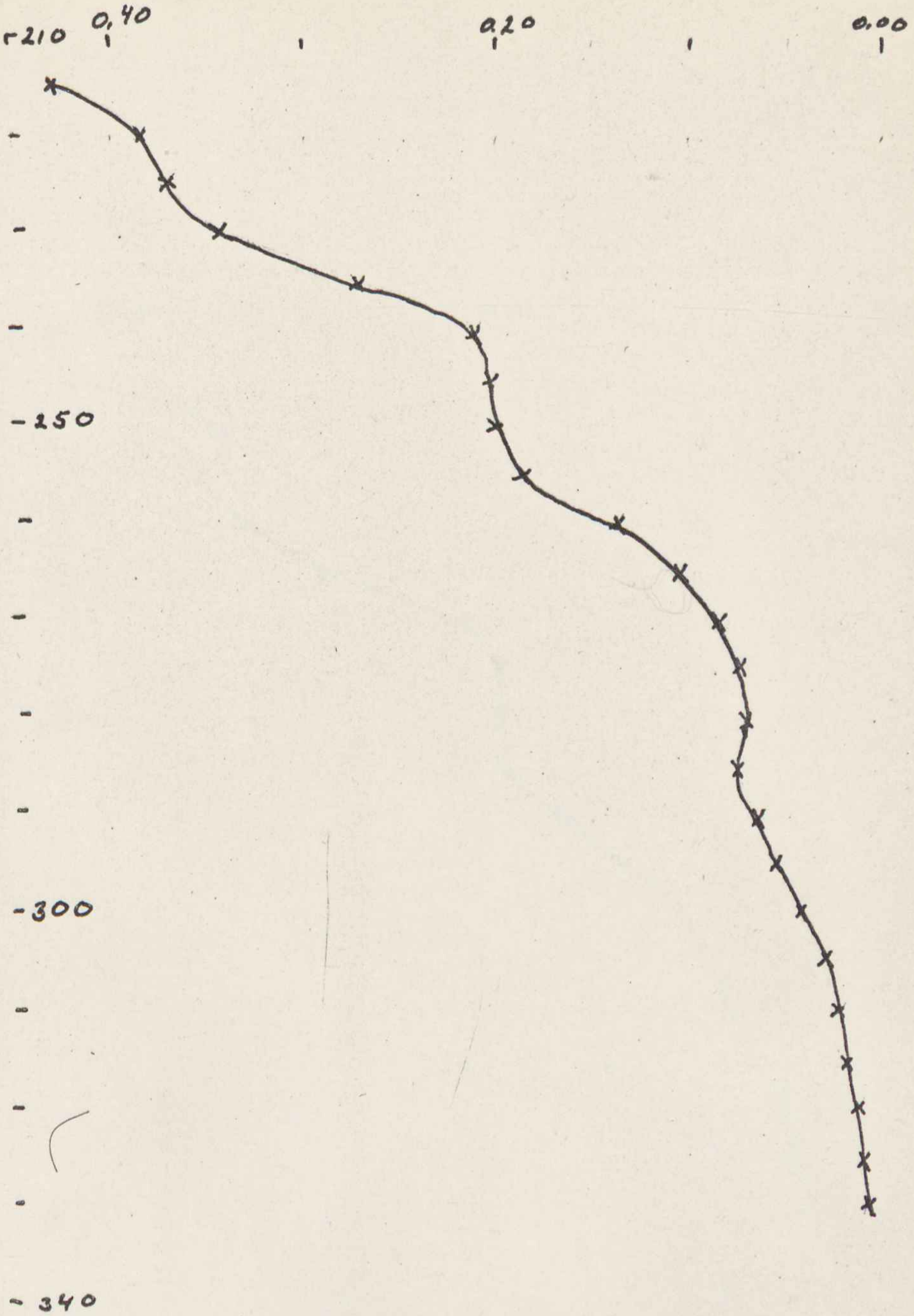
SECTIONS REMOUED FROM THIN-LAYER CHROMATOGRAM



ABSORBTION SPECTRUM OF SAMPLE AA-1

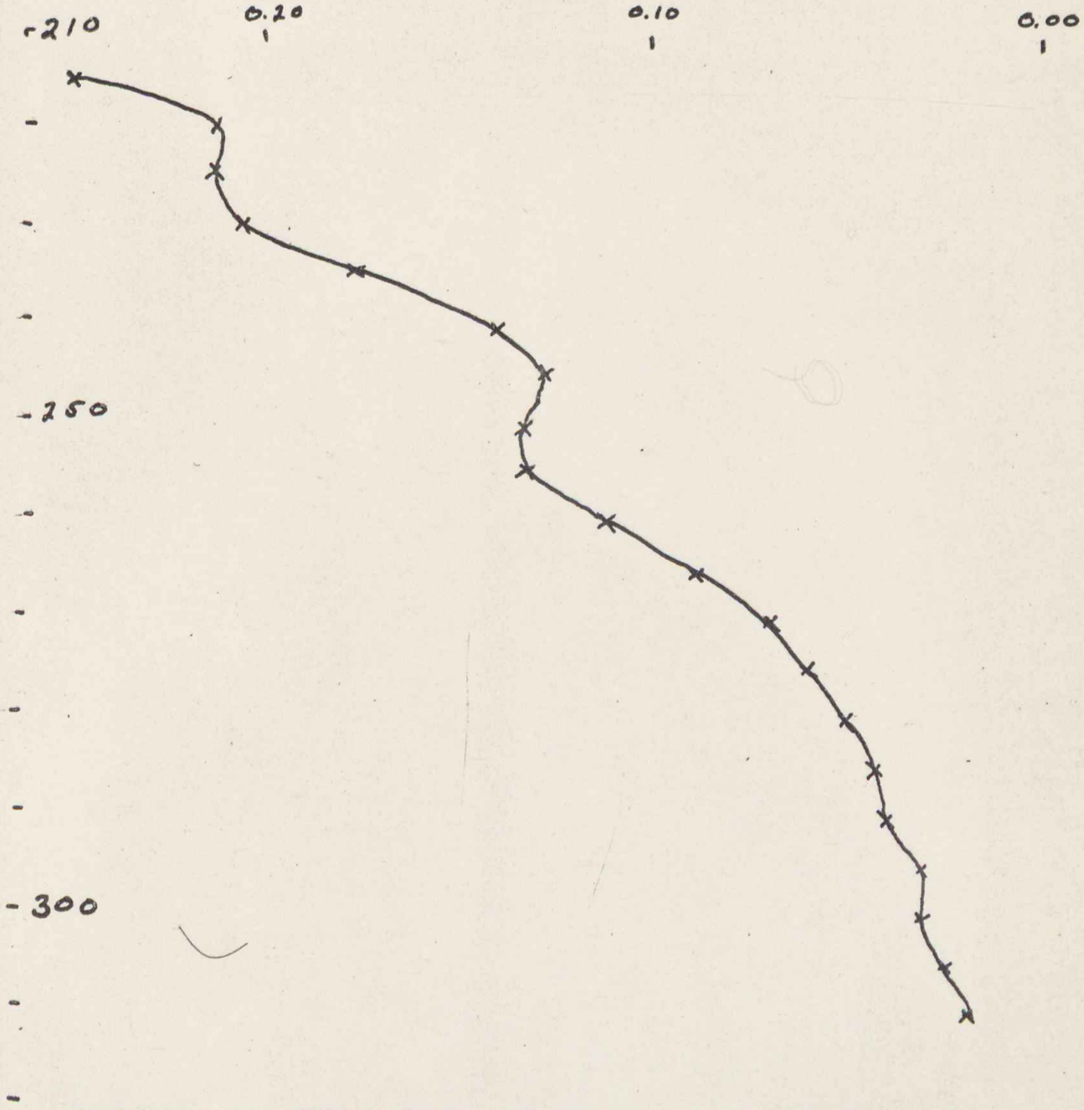
A- ORIGINAL SOLUTION DILUTED 1:5

B- ORIGINAL SOLUTION DILUTED 1:25



ABSORBTION SPECTRUM OF AA-2

ABSORBTION SPECTRUM OF SAMPLE AA-3



ABSORBTION SPECTRUM OF SAMPLE AA-BASE