[CONTRIBUTION FROM THE RESEARCH AND DEVELOPMENT DEPARTMENT, U. S. NAVAL POWDER FACTORY]

Reaction of the Acid Chlorides of Aromatic Acids with Bromine and Silver Oxide[1]

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It has been found that the acid chlorides of several aromatic acids on treatment with silver oxide and bromine in carbon tetrachloride solution loose carbon dioxide. The acid chloride is substituted by the halide.

It has been reported[3] that when the acid chlorides of acetylated hexonic acids are dissolved in carbon tetrachloride and heated at reflux temperature with silver oxide and bromine, the acid chloride loses carbon dioxide and forms the *aldehydo*-1-bromo-penta-*O*-acetyl-pentose. Either acetic anhydride or acetyl chloride[3] react with mixtures of silver oxide and bromine and after respectively losing 2 moles and 1 mole of carbon dioxide, form methyl bromide.

Although the product formed by the reaction of acid chlorides with silver oxide and bromine is essentially the same as that obtained by the decarboxylation of the silver salts of organic acids by reaction with bromine,[4] the acid chlorides, in contrast like the sugar acid chlorides, would react to form carbon dioxide and the corresponding halide.

Benzoyl chloride was found to react with silver oxide and bromine to yield bromobenzene. The *m*- and *p*-nitrobenzoyl chlorides formed the corresponding *m*- and *p*-bromonitrobenzenes. Naphthoyl chloride also reacted, although slowly, under the same conditions to form bromonaphthalene. The reaction as measured by the evolution of carbon dioxide was essentially quantitative (Table I).

A possible mechanism for the above reaction is that the acid chloride reacts with silver oxide to form the silver salt of the acid and silver chloride. The silver salt would then react with bromine to

TABLE I

DECARBOXYLATION OF AROMATIC ACID CHLORIDES WITH BROMINE AND SILVER OXIDE

Compound	Weight, g.	CO_2 evolved. Equivalent in ml. 0.1 *N* HCl Calc'd	Obsv'd	Compound[a] Isolated	M.p., °C. Observed	Literature
Benzoyl chloride	1.0	143	140	Bromobenzene	155–157 (b.p.)	155[5]
p-Nitrobenzoyl chloride[7] (m.p. 72–73)	1.95	228	211	*p*-Nitrobromobenzene	125–127	126–127[8,9]
m-Nitrobenzoyl chloride[7,11] (m.p. 32–33)	2.0	216	210	*m*-Nitrobromobenzene	56	56[10,11]
Naphthoyl chloride[12] (m.p. 52–53)	1.87	196	116	Bromonaphthalene	59	59[13]

[a] The compounds gave the correct elemental analyses.

to the silver salts are easily prepared in an anhydrous condition and hence are more convenient to use than the silver salts. We were not able to find that the decarboxylation of aromatic or aliphatic acids *via* their acid chlorides had been studied and hence it was considered of interest to investigate several aromatic acid chlorides to find out if they,

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give the product[4,5] RCOOBr which when heated would give RX + CO_2.[4,5] That the above mechanism may not be the true one, is suggested by the observation that when either the acid chloride of D-gluconic acid penta-*O*-acetate[3] or an aromatic acid chloride is added slowly to a boiling mixture of bromine and silver oxide in carbon tetrachloride, carbon dioxide is immediately and continuously evolved. On the other hand, refluxing the acid chloride with silver oxide does not lead to the immediate formation of the silver salt of the acid. On the contrary, after four hours heating only traces of silver salt can be found.

EXPERIMENTAL

Preparation of the acid chlorides from the free acid. The acid chlorides were prepared by heating the corresponding acid with thionyl chloride at reflux temperature and, after concentrating the solution to dryness under reduced pressure at room temperature, crystallizing the resulting product from petroleum ether (b.p. 30–60°). Before use the acid chlorides were dried under high vacuum at room temperature. Reagent grade benzoyl chloride was used.

Reaction of acid chloride with bromine and silver oxide. Approximately one gram of the acid chloride was dissolved in approximately 50 ml. of carbon tetrachloride in a three-neck 250-ml. flask. The carbon tetrachloride had been previously dried over phosphorus pentoxide and then redistilled. An excess amount of silver oxide (2.5 g. dried over phosphorus pentoxide in a high vacuum at 100° for 24 hours) and 2 g. of redistilled bromine in 20 ml. of dry carbon tetrachloride, was added and the mixture was stirred and heated under reflux. A stream of nitrogen from which traces of carbon dioxide had been removed by bubbling the gas through saturated aqueous sodium hydroxide and from which moisture had been removed by bubbling the gas through *conc'd* sulfuric acid was used to sweep out the carbon dioxide as it was formed. After the gases had passed through two traps immersed in Dry Ice-Acetone, to remove any trace of bromine, the carbon dioxide was absorbed in 0.2 *N* aqueous barium hydroxide. The amount of carbon dioxide evolved was determined by titrating the barium hydroxide solution with 0.1 *N* hydrochloric acid and subtracting the blank which had been run without the addition of the acid chloride, but otherwise under the same conditions. Table I shows the amount of carbon dioxide evolved from a number of acid chlorides.

The decarboxylated product was isolated by filtering the carbon tetrachloride solution, concentrating it to dryness and distilling or crystallizing the product from ethanol.

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