

with water and the reddish colored oil which soon solidified was thoroughly washed with water. After drying in a vacuum desiccator 0.55 g. of product was obtained which after two crystallizations from alcohol melted at 85.5–86°. The red color was removed by boiling the alcohol solution with a little Norit. A yield of 96.2% was obtained.

### 3. Diazotization of 2-Chloro-4-iodo-6-bromo-aniline

To 2.15 g. of the amine was added 0.5 g. of sodium nitrite, 3.5 cc. of concd. sulfuric acid and 10 cc. of ethyl alcohol. After refluxing for half an hour and evaporating the alcohol, the residue was steam distilled. One and five-tenths g. of a white crystalline substance was obtained from the distillate on cooling. After one crystallization from alcohol, the substance melted at 85.5–86.0°. The yield was 73.2%.

Mixed melting points of the halogenated benzenes obtained from the three tri-substituted anilines showed that the products were identical. The fact that the three amines gave the same compound on diazotization proves the symmetrical arrangement of the halogens.

### Summary

1. A study of the melting points of halogenated benzene derivatives shows that the melting points are raised by the introduction of additional groups except in the case of one class of compounds. Contrary to the general rule, the melting points of para dihalogenated benzene derivatives are lowered by the introduction of a group causing ortho-para substitution.

2. Symmetrical trihalogenated benzene derivatives containing iodine, bromine and chlorine in the same ring have been prepared for the first time.

3. The amino derivatives of these compounds have higher melting points than the parent hydrocarbons.

MINNEAPOLIS, MINNESOTA

---

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF WASHINGTON UNIVERSITY]

## ACTION OF THIONYL CHLORIDE ON ORGANIC ACIDS<sup>1</sup>

BY L. McMASTER AND F. F. AHMANN

RECEIVED JUNE 20, 1927

PUBLISHED JANUARY 5, 1928

Thionyl chloride is a reagent which has become very important for the synthesis of a large variety of organic compounds. In a recent article by Silberrad,<sup>2</sup> a summary of the work upon thionyl chloride is given. It is mentioned as a chlorinating and dehydrating agent, as a reagent for the removal of hydrogen from mercaptans, as a condensing agent and as a catalyst. The most frequent use of this reagent is for the conversion of an acid into its chloride, since it is easier to handle than phosphorus pentachloride. This investigation was begun some months previous to the review by Silberrad and had for its object a systematic study of the reaction of thionyl chloride on organic acids.

<sup>1</sup> This paper was presented before the Division of Organic Chemistry of the American Chemical Society, Richmond, Virginia, April 11 to 16, 1927.

<sup>2</sup> Silberrad, *J. Soc. Chem. Ind.*, **45**, 37, 55 (1926).

### Experimental Procedure

Pure acids in quantities of 15 to 25 g. were treated with two or three times their weight of pure thionyl chloride. In some cases the reaction took place immediately but usually the mixture had to be refluxed with stirring at the boiling point of the thionyl chloride to complete the reaction. In a few cases several days' refluxing were required. In most cases the acid dissolved in the thionyl chloride and a solvent was unnecessary. When a solvent was required, benzene, ether, petroleum ether, gasoline, pyridine and other inert solvents were tried. Since the by-products of the reaction are gaseous, they were readily removed and any excess thionyl chloride was distilled off. Usually the thionyl chloride replaced the OH group by Cl, forming an acid chloride, but in some cases with the dibasic acids anhydrides were formed. These products were purified either by vacuum distillation or by crystallization. In cases where acids were found not to react, various catalyzers such as pyridine, aluminum chloride and iodine were tried.

TABLE I

#### SUBSTITUTED ACETIC ACIDS

Acid	Amt. in g.	Time, hours	Product	% Yield
Chloro-acetic	15	24	Monochloro-acetyl chloride	55
Trichloro-acetic	15	48	None	..
Amino-acetic	12	12	None	..

The three negative chlorine groups in trichloro-acetic acid evidently prevent the formation of an acid chloride. With the amino-acetic acid a reaction took place and the thionyl chloride turned intensely red but we were unable to isolate any products of the reaction. It is probable that the amino group was attacked.

TABLE II

#### ALIPHATIC DIBASIC ACIDS

Acid	Amt. in g.	Time, hours	Product	% Yield
Oxalic	15	72	None	..
Malonic	15	2	Malonyl chloride	60
Succinic	20	6	Succinic anhydride	78
Glutaric	15	6	Glutaric anhydride	78

It was thought that thionyl chloride might react with diethyl oxalate to form oxalyl chloride, but no reaction took place upon refluxing the mixture for forty-eight hours. This is the only method by which malonyl chloride can be prepared, since phosphorus pentachloride converts malonic acid into carbon suboxide. It is a liquid which distils at 55° (15 mm.) and turns dark red on standing. The literature records that succinic anhydride can best be made by this method. Suberic and sebacic acids are reported<sup>3</sup> as forming dichlorides.

<sup>3</sup> Hans Meyer, *Monatsh.*, **22**, 415, 777 (1901).

### The Hydroxy Acids

The action of this reagent on the hydroxy acids has not been studied very extensively. Malic acid is mentioned as forming a dichloride, while no reference is made to tartaric acid. Lactic acid yields a variety of products.<sup>4</sup> Tartaric acid is the only one of this group studied by us. 15 g. of the acid was refluxed for several days with 40 cc. of thionyl chloride without any result. No suitable solvent for the acid could be found in which to carry out the reaction.

### Unsaturated Dibasic Acids

Fumaric, mesaconic and bromomaleic acids are described<sup>5</sup> as forming dichlorides, while maleic, citraconic and itaconic acids form anhydrides. We obtained a 90% yield of maleic anhydride but could not get fumaric acid to react. Benzene, petroleum ether and pyridine were used as solvents without success. We intend to repeat the action of thionyl chloride on the other unsaturated dibasic acids mentioned, since our work does not agree with the results given in the literature.

TABLE III  
SUBSTITUTED BENZOIC ACIDS  
15 g. of acid used in each case

Acid	Time, hours	Product	% Yield
<i>o</i> -Nitrobenzoic	3	<i>o</i> -Nitrobenzoyl chloride	90
<i>m</i> -Nitrobenzoic	3	<i>m</i> -Nitrobenzoyl chloride	86
<i>p</i> -Nitrobenzoic	6	<i>p</i> -Nitrobenzoyl chloride	73
<i>o</i> -Aminobenzoic	3	None	..
<i>m</i> -Aminobenzoic	3	<i>m</i> -Aminobenzoyl chloride	83
<i>p</i> -Aminobenzoic	4	<i>p</i> -Aminobenzoyl chloride	88

Heumann and Koechlin<sup>5</sup> studied the action of thionyl chloride on benzoic acid. We obtained a 98% yield against one of 90% by the phosphorus pentachloride method. Meyer<sup>6</sup> has prepared by this method the *p*-nitrobenzoyl chloride after a long period of refluxing. We found that it was the most difficult of the three to prepare.

Phosphorus pentachloride cannot be used to prepare an acid chloride of an aminobenzoic acid since it attacks the amino group. We could find no references to the acid chlorides of the aminobenzoic acids. In the case of the *o*-aminobenzoic acid a vigorous reaction took place when it was first treated with the thionyl chloride and it was necessary to surround the flask with a freezing mixture. We were not able to isolate any definite products of the reaction. The *m*-aminobenzoyl chloride is a yellow oil distilling at 125° (15 mm.). Upon standing it passes into a solid of m. p. 42° and possesses a decided acid chloride odor. It reacts vigorously with

<sup>4</sup> Frankland and Garner, *J. Chem. Soc.*, **105**, 1101 (1914).

<sup>5</sup> Heumann and Koechlin, *Ber.*, **16**, 1625 (1883).

<sup>6</sup> Hans Meyer, *J. Chem. Soc.*, **80**, 1, 628 (1901); **82**, 1, 31 (1902).

water, ammonia and alcohol. Analysis gave 22.72% of chlorine whereas the calculated value is 23.44%. The *p*-aminobenzoyl chloride is also a yellow oil distilling at 120° (12 mm.), solidifying upon standing to yellow crystals of m. p. 31°. These crystals possess the same properties as the meta compound and were found to contain 22.62% of chlorine.

### The Hydroxybenzoic Acids

In only exceptional cases have the acid chlorides of the hydroxybenzoic acids been prepared by ordinary methods. When phosphorus pentachloride is used as a chlorinating agent, the OH group is also attacked. Meyer found that salicylic acid, *m*-hydroxybenzoic acid and *o*- and *m*-cresotinic acids readily formed the acid chlorides with thionyl chloride. We were able to obtain by using the free acid only a very small yield of the acid chloride of salicylic acid but a 36% yield was obtained by using the sodium salt of the acid. The salicylyl chloride is a white, crystalline substance melting at 18° to a colorless, sirupy liquid which distills at 90° (11 mm.). No yield of the acid chloride could be obtained with *m*-hydroxybenzoic acid nor with *o*- and *m*-cresotinic acids as claimed by Meyer. We obtained only glassy solids of indefinite composition. The para acids do not react. Meyer states that an acid chloride is not formed if the acid has an OH group in the para position unless a second OH group is in the ortho position with respect to the first OH group.

### The Phthalic Acids

The phthalic acids have been studied previously by Meyer, who found that phthalic acid formed an anhydride, isophthalic acid a dichloride and terephthalic acid was unattacked. Since no yields were recorded they were reinvestigated.

TABLE IV

THE PHTHALIC ACIDS				
Acid	Amt. in g.	Time, hours	Product	% Yield
Phthalic	20	2	Phthalic anhydride	95
Isophthalic	10	12	Isophthalyl chloride	62
Terephthalic	15	72	None	..

Attempts to prepare phthalyl chloride were made by prolonged boiling of the anhydride with the thionyl chloride using aluminum chloride, iodine and pyridine as catalysts but without success. The isophthalyl chloride is a colorless oil distilling at 200° (15 mm.). Catalysts and various inert solvents were tried in the attempt to prepare terephthalyl chloride.

### Summary

1. Thionyl chloride readily converts the acids of the fatty acid series into acid chlorides. Chloro-acetic acid is converted into an acid chloride while trichloro-acetic and amino-acetic acids are not.

2. Of the dibasic acids, oxalic is unattacked, while succinic and glutaric yield anhydrides and malonic, suberic and sebacic acids form dichlorides.
3. Tartaric acid is unattacked.
4. Of the unsaturated dibasic acids employed, maleic forms an anhydride and fumaric acid is unchanged.
5. Of the benzoic acids, the three nitrobenzoic acids all form the acid chlorides. The *p*-nitrobenzoyl chloride is formed only with difficulty due to the presence of the negative nitro group in the para position. Acid chlorides of *m*- and *p*-aminobenzoic acid can be prepared by this method. The ortho acid does not form an acid chloride.
6. Only by the use of thionyl chloride can the acid chlorides of some of the aromatic hydroxy acids be prepared. *o*-Hydroxybenzoic acid forms an acid chloride while the para acid does not. *m*-Hydroxybenzoic acid and the cresotinic acids gave products which could not be identified as acid chlorides as stated by Meyer.
7. Of the phthalic acids, the ortho acid forms an anhydride, the meta acid a dichloride and the para acid is not attacked by thionyl chloride.
8. The action of thionyl chloride on other organic acids is being continued in this Laboratory.

ST. LOUIS, MISSOURI

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

## THE HEXAPHENYLETHANE ALKYL SULFIDE ADDITION COMPOUNDS<sup>1</sup>

BY VICTOR C. ROGERS<sup>2</sup> AND GREGG DOUGHERTY

RECEIVED JUNE 27, 1927

PUBLISHED JANUARY 5, 1928

### Introduction

Hexaphenylethane (triphenylmethyl) possesses the property of forming addition products with a great variety of organic substances.<sup>3,4</sup> The majority of these addition products have a composition corresponding to the ratio of one mole of hexaphenylethane to one mole of the substance added. In the case of the additions involving esters, ethers and ketones,<sup>5</sup> the oxonium theory is probably applicable, as follows



<sup>1</sup> This article is based upon a thesis submitted by Victor C. Rogers to the Faculty of the Graduate School of Princeton University in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

<sup>2</sup> DuPont Fellow in Chemistry.

<sup>3</sup> Pfeiffer, "Organische Molekülverbindungen," F. Enke, Stuttgart, 1922, p. 250.

<sup>4</sup> Schmidlin, "Das Triphenylmethyl," F. Enke, Stuttgart, 1914, p. 75.

<sup>5</sup> (a) Gomberg, *Ber.*, **34**, 2730 (1901); (b) **38**, 2449 (1905).