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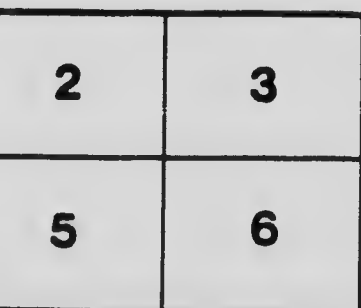
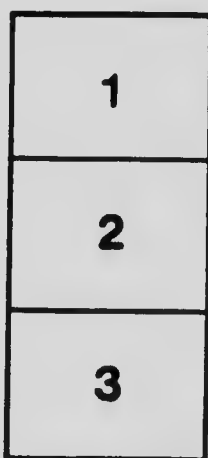
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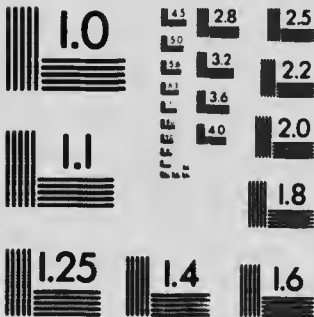
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STUDIES**

**PAPERS FROM THE CHEMICAL  
LABORATORIES**

**No. 113: FRIEDEL AND CRAFTS' REACTION — NITRO-  
PHTHALIC ANHYDRIDES AND ACETYLAMINO-PHTHALIC  
ANHYDRIDES WITH BENZENE AND ALUMINUM CHLOR-  
IDE, BY W. A. LAWRENCE**

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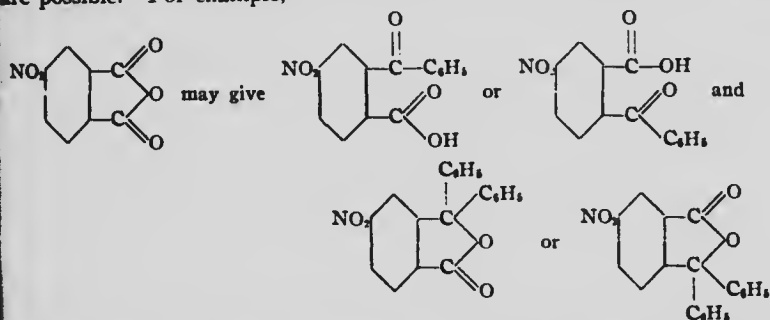
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**FRIEDEL AND CRAFTS' REACTION—NITRO-PHTHALIC ANHY-  
DRIDES AND ACETYLAMINO-PHTHALIC ANHYDRIDES  
WITH BENZENE AND ALUMINUM CHLORIDE.**

BY WALTER A. LAWRENCE.

Received June 16, 1920.

In Friedel and Crafts'<sup>1</sup> synthesis of *o*-benzoylbenzoic acid, phthalic anhydride is heated with benzene and aluminum chloride. This reaction has been studied quantitatively by Rubidge and Qua,<sup>2</sup> who state the conditions under which a 97% yield may be obtained and also the conditions which give a good yield of diphenyl-phthalide.

The object of the present research was to study this reaction when the 2 nitro-phthalic anhydrides and the 2 acetylaminophthalic anhydrides were used. When a substituted phthalic anhydride is treated with benzene and aluminum chloride 2 acids and 2 derivatives of diphenyl-phthalide are possible. For example,



In most of the reactions studied the yields of the acids were poor, and in only one case was any attempt made to alter the conditions of the experiment in order to obtain the derivatives of diphenyl-phthalide.

The literature on this subject is confined to 2 papers by Rainer.<sup>3</sup> From 4-nitro-phthalic anhydride, this investigator obtained 2-benzoyl-4-nitrobenzoic acid identical with that obtained by Kliegl<sup>4</sup> from phenyl-nitrofluorene and 6-benzoyl-3-nitrobenzoic acid, m. p. 212°. Rainer also describes the reduction of the latter acid to 6-benzoyl-3-aminobenzoic acid, m. p. 193-4°. The products obtained separately by Rainer and Kliegl are identical with those obtained by the author from 4-acetylaminophthalic anhydride.

In this work, the acetylaminophthalic anhydrides were used instead

<sup>1</sup> *Ann. chim. phys.*, [6] 14, 446 (1888).

<sup>2</sup> Rubidge and Qua, *THIS JOURNAL*, 36, 732 (1914).

<sup>3</sup> Rainer, *Monatsh.*, 29, 178; 29, 431 (1908).

<sup>4</sup> Kliegl, *Ber.*, 38, 294 (1905).



of the amino compounds because of the difficulty of preparing the amino anhydrides from the corresponding acids and also because of the general difficulty of using unprotected amines in the Friedel and Crafts' reaction.

**Preparation of Nitro-phthalic Acids.**—Several methods of preparing nitrophthalic acids have been described. Beilstein and Kurbatow<sup>1</sup> nitrated naphthalene and oxidized the product, Miller<sup>2</sup> nitrated phthalic acid and May,<sup>3</sup> Edinger,<sup>4</sup> and Poupold<sup>5</sup> obtained nitrophthalic acids by nitration of phthalic anhydride. Bogert and Boroschek,<sup>6</sup> using the latter method, increased the yield of 3-nitro-phthalic acid from 25% to 38% by renitration. In the method described below larger quantities of the mixed acids are used and renitration is unnecessary. A mixture of 125 g. of nitric acid (sp. gr. 1.5) and 125 g. of sulfuric acid (sp. gr. 1.834) was cooled and put in a 2-liter flask containing 50 g. of phthalic anhydride. The flask was heated gently on a water-bath until the temperature reached 75°, and then removed. Vigorous nitration began at about 80° and the flask was kept at about 100° for 3 hours, then allowed to cool, and the contents was poured into an equal volume of water. After standing overnight the precipitated acids were collected on a filter and the 3-nitro-phthalic acid was obtained by recrystallization of the product from hot water. The mother liquor was concentrated and 4-nitro-phthalic acid extracted with ether. The 4-nitro-phthalic acid may be purified by dissolving it in 95% alcohol and gradually adding benzene to the solution; but the method described by Bogert and Boroschek was found to give a purer product. This preparation gave a yield of 42% of the 3-nitro-phthalic acid and 47% of the 4-nitro-phthalic acid.

**Preparation of 3-Nitro-phthalic Anhydride.**—Bogert and Boroschek heated 3-nitro-phthalic acid for from 6 to 8 hours at 235–240° and obtained the anhydride in good condition. Kahn<sup>7</sup> gave 218° as the maximum temperature to be used, but later<sup>8</sup> used 230°. Bogert's experiment, repeated, gave considerable tarry material, and the product melted at 162–4°. The method finally adopted was to put the acid into a small flask and heat it in an air-oven at 215–7° (thermometer bulb in the melt) from 3 to 4 hours. When recrystallized from glacial acetic acid, the anhydride had a very pale yellow-brown color and melted sharply at 164°. Yield, about 89%. Quantitative determinations showed that at 215° the anhydride was slowly volatilized.

<sup>1</sup> Beilstein and Kurbatow, *Ann.*, 202, 217 (1880).

<sup>2</sup> Miller, *ibid.*, 208, 223 (1881).

<sup>3</sup> May, *Inaug. Dissertation*, Frieberg, 1880.

<sup>4</sup> Edinger, *J. prakt. Chem.*, [2] 53, 382 (1895).

<sup>5</sup> Poupold, *Inaug. Dissertation*, Basle, 1897.

<sup>6</sup> Bogert and Boroschek, *THIS JOURNAL*, 23, 743 (1902).

<sup>7</sup> Kahn, *Ber.*, 35, 472 (1902).

<sup>8</sup> *Ibid.*, 35, 3859 (1902).

**Preparation of 4-Nitro-phthalic Anhydride.**—A quantity of 4-nitro-phthalic acid was heated in a small flask, in an air-oven, at  $165-8^{\circ}$ , for about 3 hours. The product, when cooled, was at first a brown gummy mass, but it slowly crystallized on standing. It was recrystallized first from acetyl chloride and then from glacial acetic acid. M. p.,  $114^{\circ}$ . Yield, 80%. This anhydride is volatile at  $165^{\circ}$ .

**Preparation of the Mono-ethyl Esters of 3-Nitro-phthalic Acid.**—A solution of 3-nitro-phthalic acid in absolute ethyl alcohol was saturated with hydrogen chloride and boiled for one hour under a reflux condenser. The ester, when recrystallized, melted at  $110^{\circ}$ . This ester is 2-carbethoxy-3-nitrobenzoic acid.<sup>1</sup>

When 3-nitro-phthalic anhydride was dissolved in absolute ethyl alcohol and boiled for 5 hours, the isomeric ethyl ester, 6-carbethoxy-2-nitrobenzoic acid, was formed.<sup>2</sup> M. p.  $156-7^{\circ}$ .

**Preparation of 3-Acetyl-amino-phthalic Anhydride.**—As interest lay only in the acetyl derivative of the amino-phthalic anhydride, it was found more convenient to prepare this compound directly from the hydrochloride of the amine. Bogert and Jouard<sup>3</sup> obtained the hydrochloride of 3-amino-phthalic acid by reduction of the nitro acid with stannous chloride and recrystallization of the product from hot conc. hydrochloric acid. They also prepared the acetyl derivative from the amine and from the hydrochloride by using acetic anhydride, but gave no details.

Forty g. of 3-nitrophthalic acid was finely powdered and gradually added to 325 cc. of stannous chloride solution (150 g. of stannous chloride, 250 cc. of conc. hydrochloric acid and 50 cc. water) while the mixture was stirred thoroughly. The temperature of the reducing solution was kept at about  $22^{\circ}$  and the acid went slowly into solution. A short time after complete solution was effected the hydrochloride was precipitated slowly as a white voluminous substance. After several hours the precipitate was collected and the filtrate saturated with hydrogen chloride, which produced more of the precipitate. The product was recrystallized from hot conc. hydrochloric acid and dried, *in vacuo*, over both sulfuric acid and sodium hydroxide. Miller<sup>4</sup> states that he obtained a double tin salt by reduction of 3-nitro-phthalic acid with stannous chloride and based his formula on a chlorine determination; later<sup>5</sup> he modified this to conform with additional analyses. Bogert and Jouard state that they found no trace of a double salt. In one of our preparations this double salt was obtained, and investigation showed that the temperature was the controlling

<sup>1</sup> *Ann.*, 208, 223 (1881).

<sup>2</sup> *THIS JOURNAL*, 23, 746 (1901).

<sup>3</sup> Bogert and Jouard, *ibid.*, 31, 485 (1909).

<sup>4</sup> Miller, *Ber.*, 11, 994 (1878).

<sup>5</sup> *Ann.*, 208, 223 (1881).

factor; at about  $22^{\circ}$ , no tin salt was obtained, but when the reducing solution was allowed to become hot (sometimes  $75^{\circ}$  was reached) the double salt was found.

Twenty g. of the dry hydrochloride was dissolved in 80 cc. of acetic anhydride and boiled for 5 minutes. The acetyl-amino-phthalic anhydride crystallized when the solution was cooled, and was recrystallized from alcohol. M. p.  $185-6^{\circ}$ . Yield, 55%, calculated from the nitro compound.

**Preparation of 4-Acetyl-amino-phthalic Anhydride.**—The direct reduction of 4-nitro-phthalic acid with stannous chloride gives a double tin salt. When tin is precipitated by hydrogen sulfide this compound is converted into aminobenzoic acid with loss of carbon dioxide. Several indirect methods of preparing the amino acid have been proposed,<sup>1</sup> the one used below is that given by Bogert and Renshaw.<sup>2</sup>

The acid ammonium salt of 4-nitro-phthalic acid was converted into the imide and the nitro-imide reduced with stannous chloride. The amino-phthalimide, when boiled with ammonia, gave the ammonium salt of amino-phthalic acid from which the free acid was liberated by addition of hydrochloric acid. The 4-amino-phthalic acid was dissolved in acetic anhydride, boiled for a few minutes, allowed to cool and the acetyl-amino-phthalic anhydride filtered off. The product, recrystallized from ethyl acetate and acetyl chloride, did not have a sharp melting-point ( $203-6^{\circ}$ ). The yield was less than 10%, calculated on the acid ammonium salt.

### 3-Nitrophthalic Anhydride with Benzene and Aluminum Chloride.

Because of the slight solubility of the anhydride in benzene, a larger excess of this reagent was used. A mixture of 100 cc. of benzene and 6.5 g. of 3-nitro-phthalic anhydride (finely powdered) was put in a 300-cc. flask attached to a reflux condenser and boiled for a few minutes on the water-bath. After cooling the product, 9.0 g. of powdered aluminum chloride was added slowly while the flask was shaken at intervals. The mixture darkened rapidly and soon assumed a deep brown color. Then it was heated on the water-bath until hydrogen chloride ceased to escape, which usually required about 4 or 5 hours. When the mixture became cold, 80 cc. of 10% hydrochloric acid was added and the excess of benzene was distilled with steam. The solution was cooled to  $15^{\circ}$  and filtered to remove the black gummy mass. The filtrate, evaporated to half its volume and extracted twice with ether, gave 3-nitro-phthalic acid equivalent to 55-60% of the anhydride used.

The black residue from the reaction was thoroughly agitated with a warm 5% solution of sodium hydroxide and filtered from the insoluble

<sup>1</sup> *Ber.*, 34, 4352 (1901); *J. Chem. Soc.*, 87, 1269 (1905).

<sup>2</sup> Bogert and Renshaw, *This Journal*, 30, 1137 (1908).

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portion. The filtrate contained the 2 possible benzoyl-nitrobenzoic acids as sodium salts, from which the free acids were obtained by the addition of 5% hydrochloric acid. The hydrochloric acid was added very slowly and at intervals of several hours; otherwise the precipitate was a gummy mass which made subsequent operations difficult. The 2 constituents of this precipitate have different solubilities in cold 95% alcohol, but the separation by acetic acid was found better than fractional crystallization from alcohol.

Hot 80% acetic acid dissolved one of these constituents and only a trace of the other. The acetic acid solution was filtered while hot, water was added until a faint cloudiness appeared, and after the solution had stood overnight, the precipitate was filtered off and dried. It softens at  $140^{\circ}$  and melts, with decomposition, at  $158-61^{\circ}$ . The portion insoluble in acetic acid melts with decomposition at  $217-21^{\circ}$ .

**Identification of the Portion Insoluble in Acetic Acid.**—*Hydrolysis.*—The finely divided substance was added to molten potassium hydroxide contained in a nickel dish and the temperature was kept a few degrees above the fusion point for from one to two hours. Then the mass was dissolved in water, acidified with hydrochloric acid, washed, and kept in a vacuum-oven at  $100^{\circ}$  until the residue had a constant melting-point,  $146-8^{\circ}$ —that of *o*-nitrobenzoic acid. The sublimate was benzoic acid.

*Synthesis.*—(A convenient method of preparation.) Ten g. of 2-carboethoxy-3-nitrobenzoic acid was dissolved in 15 cc. of thionyl chloride and kept at  $60-70^{\circ}$  until hydrogen chloride and sulfur dioxide were no longer given off. The excess thionyl chloride was then removed by distillation under reduced pressure. The resulting acid chloride is a light brown crystalline substance, is soluble in benzene and in ether, melts at  $76-7^{\circ}$ . To a solution of 8.4 g. of the acid chloride in 50 cc. of benzene, 9 g. of powdered aluminum chloride was added slowly. When the initial reaction had ceased, the flask was heated on the water-bath until the evolution of hydrogen chloride ceased. After acidification, the benzene was distilled with steam and the precipitate saponified with alcoholic potassium hydroxide. Water and hydrochloric acid were added which caused the precipitation of a light brown crystalline substance that melted with decomposition at  $220-1^{\circ}$  and was identical with the substance described above as insoluble in acetic acid. Yield, 45%, calculated on the acid chloride used.<sup>1</sup>

This method of synthesis and the products of hydrolysis leave no doubt that the acid is 6-benzoyl-2-nitrobenzoic acid.

Calc. for  $C_{16}H_9O_4N$ : N, 5.16. Found: 5.10.

<sup>1</sup> Mr. M. E. Smith is working on the use of ester acid chlorides in Friedel and Crafts' reaction, in this laboratory.

The acid is soluble in alcohol, acetone, and in pyridine and slightly soluble in ether and in benzene.

**Identification of the Portion Soluble in Acetic Acid.**—*Hydrolysis.*—The products of hydrolysis by potassium hydroxide were *m*-nitrobenzoic acid and benzoic acid.

*Synthesis.*—The acid was made from 6-carbethoxy-2-nitrobenzoic acid, according to the method described above. The acid chloride obtained is a yellowish oily liquid miscible with benzene and with ether. It decomposes above 100°. The acid obtained melted with decomposition at 157–60°, was identical with the above portion soluble in acetic acid, and is 2-benzoyl-3-nitrobenzoic acid. It is very soluble in acetone and slightly soluble in ether, in alcohol and in water.

The yields of benzoyl-nitrobenzoic acids obtained when 3-nitro-phthalic anhydride reacts with benzene and aluminum chloride are very low. From 6.5 g. of the anhydride about 3.8 g. was recovered as 3-nitro-phthalic acid and about 1.7 g. of a black resinous substance insoluble in sodium hydroxide and also insoluble in the usual organic solvents. Approximately 0.7 g. of 6-benzoyl-2-nitrobenzoic acid and 0.6 g. of 2-benzoyl-3-nitrobenzoic acid were obtained. Various modifications were made in the method but neither the use of freshly distilled aluminum chloride, nor the addition of carbon disulfide as a diluent, nor an excess of aluminum chloride produced any better yields. If heat was applied longer than 5 hours the resinous product increased and the recovered 3-nitro-phthalic acid decreased, but the yield of benzoyl-nitrobenzoic acids was not improved.

#### 4-Nitro-phthalic Anhydride with Benzene and Aluminum Chloride.

The method used was similar to that described for 3-nitro-phthalic anhydride. Separation of the 2 benzoyl-nitrobenzoic acids was made by the use of methyl alcohol as described by Rainer. One isomer, 6-benzoyl-3-nitrobenzoic acid, m. p. 212°, recrystallizes from the methyl alcohol while the more soluble isomer, 2-benzoyl-4-nitrobenzoic acid, m. p. 164–5°, is obtained by concentrating the alcoholic solution. With 6.5 g. of 4-nitro-phthalic anhydride dissolved in 100 cc. of benzene and 9 g. of aluminum chloride, about 0.8 g. of 6-benzoyl-3-nitrobenzoic acid and 0.5 g. of 2-benzoyl-4-nitrobenzoic acid were produced while 50% of the anhydride was recovered as 4-nitro-phthalic acid. The brown resinous substance, insoluble in sodium hydroxide, formed in the reaction, gave positive test for nitrogen and left a small ash on ignition.

#### 3-Acetyl-amino-phthalic Anhydride with Benzene and Aluminum Chloride.

A mixture of 6.8 g. of 3-acetyl-amino-phthalic anhydride and 50 cc. of benzene was placed in a 200 cc. flask and boiled under a reflux condenser for several minutes. This solution was cooled and 9 g. aluminum

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chloride was slowly added while the contents of the flask was shaken thoroughly to prevent caking. The reaction was carried out on the water-bath until hydrogen chloride was no longer evolved, when 60 cc. of 10% hydrochloric acid was added and the benzene was distilled with steam. The distillation with steam removes the acetyl radical. The precipitate was shaken with a hot saturated solution of sodium carbonate and filtered from the brownish insoluble material. Slow addition of 5% hydrochloric acid to the filtrate gave a crystalline precipitate which, when recrystallized from ethyl alcohol, was white and melted at 193-4°. Yield, 51% calculated on the basis of the 3-acetylamino-phthalic anhydride used. The alcohol solution evaporated to dryness gave a small quantity of a pale yellow crystalline substance which melted at 159-60° when recrystallized from water.

**Identification of the Substance Melting at 193-4°.—Hydrolysis.**—Hydrolysis with potassium hydroxide was not very successful; the only product that could be identified was benzoic acid.

**Preparation by Reduction of the Nitro Compound.**—To a solution of 2 g. of 2-benzoyl-3-nitrobenzoic acid in a small quantity of ammonia, 12 g. of ferrous sulfate and more ammonia were added. At first this was heated gently and then it was boiled for a few minutes. Six g. of charcoal was added and it was boiled again for a few minutes before it was filtered. The black precipitate was boiled with water for about 10 minutes. After the residue had been removed the filtrate was boiled until all free ammonia was expelled; then powdered potassium alum was added, and the mixture was allowed to stand until it became cold. The precipitate formed was dried, boiled with 95% alcohol, and the solution filtered hot. The crystals separated from the cold alcoholic solution were identical with those obtained in the Friedel and Crafts reaction,

Calc. for  $C_{14}H_{11}O_3N$ : N, 5.81. Found: 5.74.

This substance melting at 193-4° is, therefore, 2-benzoyl-3-amino-benzoic acid. It is slightly soluble in water, in ether and in benzene, and soluble in hot alcohol.

**Identification of the Substance Melting at 159-60°.**—As a very small quantity of this substance was obtained, it was not possible to make a nitrogen determination. On so small a scale, fusion with potassium hydroxide was not successful, but the substance was prepared from 6-benzoyl-2-nitrobenzoic acid by the method described above. Since this acid is soluble in hot water, the aluminum hydroxide was filtered from the hot solution. Crystals separated from the cold solution gave a melting-point of 159-60°. Therefore, this pale yellow substance is 6-benzoyl-2-amino-benzoic acid. It is insoluble in benzene but soluble in alcohol, in ether, in acetone, and in hot water.

**Identification of the Substance Insoluble in Hot Sodium Carbonate Solution.**—This brown material from the Friedel and Crafts reaction is

very soluble in alcohol, in ether and in benzene. It was purified from solution in alcohol to which water was added carefully until a slight turbidity appeared; after several hours, a few pale salmon-colored crystals appeared; these melted at  $130^{\circ}$ . Some hours later, an orange-colored amorphous powder (m. p.  $86-89^{\circ}$ ) was obtained from the alcoholic solution. Efforts to obtain a product with a sharper melting-point were without success.

In this Friedel and Crafts reaction, two diphenylamino-phthalides might be formed which we may call diphenyl-3-amino-phthalide and diphenyl-6-aminophthalide. The experiment was repeated under conditions shown by Rubidge and Qua to be favorable to an increased production of phthalides. Thus, 6.8 g. of 3-acetylamino-phthalic anhydride, 50 cc. of benzene and 9 g. of aluminum chloride were heated on the water-bath for 7 hours; then 10 cc. of acetic anhydride was added and the heating was continued for another 7 hours. The principal product obtained was an orange-colored gummy substance which, when crystallized from alcohol, was identical with the previous product, m. p.  $86-9^{\circ}$ . No trace of the substance melting at  $130^{\circ}$  was found. This compound is either diphenyl-3-amino-phthalide or diphenyl-6-amino-phthalide.

Calc. for  $C_{20}H_{15}O_2N$ : N, 4.65. Found: 4.47.

The yield of this phthalide was 11% in the original experiment and 31% when acetic anhydride was used, calculated on the basis of 3-acetylamino-phthalic anhydride.

#### 4-Acetylamino-phthalic Anhydride with Benzene and Aluminum Chloride.

A mixture of 5 g. of 4-acetylamino-phthalic anhydride (crude) and 50 cc. of benzene was boiled for a few minutes, then cooled and 6.75 g. of aluminum chloride was added slowly while the mixture was well shaken. The reaction was carried out at  $80-85^{\circ}$  until hydrogen chloride was no longer evolved, and the solution was then allowed to cool. To this product 50 cc. of 10% hydrochloric acid was added and the excess of benzene was distilled with steam. When cold, the residue was filtered, boiled with a saturated solution of sodium carbonate and the solution filtered from the small quantity of gummy insoluble matter. Hydrochloric acid was added slowly to the filtrate and a pale yellow precipitate was obtained which, when washed with ice-water and dried, melted at  $183-4^{\circ}$ . Separation of the 2 benzoyl-amino benzoic acids was accomplished by fractional crystallization from water. After 3 recrystallizations, 2 fractions were isolated, one melting at  $193-4^{\circ}$  and the other, at  $195-6^{\circ}$  (with decomposition).

Rainer<sup>1</sup> obtained a benzoyl-aminobenzoic acid by reduction of "o-benzoyl-m-nitrobenzoic acid;" it melted at  $193-4^{\circ}$ . This is identical with one of the acids obtained from the above reaction and is 6-benzoyl-3-

<sup>1</sup> *Monatsh.*, 29, 431 (1908).



aminobenzoic acid. Kliegl<sup>1</sup> reduced "*o*-benzoyl-*p*-nitrobenzoic acid" (which he obtained from phenylnitro-fluoren) and isolated a product which melted at 195° with decomposition. This isomeric compound is 2-benzoyl-4-aminobenzoic acid and is the other acid obtained by the Freidel and Crafts reaction.

#### Summary.

1. The reactions of aluminum chloride and benzene with 3-nitro-phthalic anhydride, 4-nitro-phthalic anhydride, 3-acetylamino-phthalic anhydride and 4-acetylamino-phthalic anhydride, respectively, have been studied and the 2 possible derivatives of benzoylbenzoic acid have been obtained in each case.

2. In only one reaction was a derivative of diphenyl-phthalide isolated and, in this instance, Rubidge and Qua's method for increasing the yield of phthalide gave good results.

3. Seven new compounds have been prepared:

	M. p.
6-Benzoyl-2-nitrobenzoic acid.....	220-21° (decomp.)
2-Benzoyl-3-nitrobenzoic acid.....	157-60° (decomp.)
6-Benzoyl-2-aminobenzoic acid.....	159-60°
2-Benzoyl-3-aminobenzoic acid.....	193-4°
Diphenyl-?-amino-phthalide.....	86-9°
2-Carbethoxy-3-nitrobenzoyl chloride.....	76-7°
6-Carbethoxy-2-nitrobenzoyl chloride.....	Oil

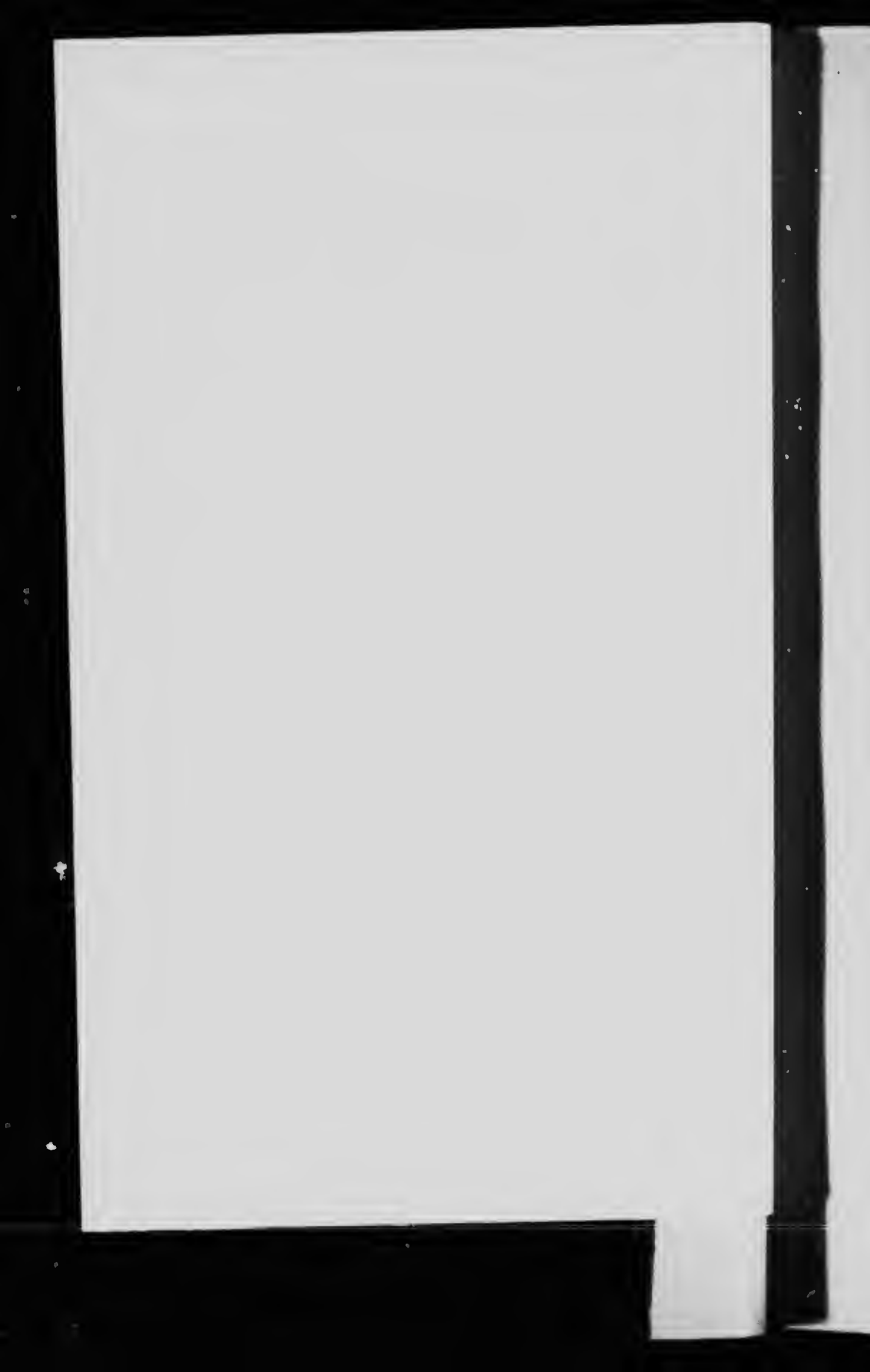
4. Detailed directions are given for the preparation of several of the compounds used in the experiments and an improved method for the preparation of the benzoyl-3-aminobenzoic acids.

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TORONTO, CANADA.

<sup>1</sup> Ber., 38, 296 (1905).





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