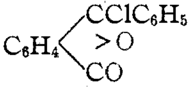
ORTHOBENZOYL-BENZOYL CHLORIDE.

By H. C. Martin.

Received March 16, 1916.

o-Benzoyl-benzoic acid has been represented by two tautomeric formulas. The necessity for this was based on the behavior of the acid chloride.

Haller and Guyot[1] prepared *o*-benzoyl-benzoyl chloride by treating the anhydrous acid with phosphorus pentachloride in carbon disulfide. Large colorless crystals were obtained melting about 70°. They suggested the formula  $C_6H_4\left\langle\begin{matrix}CClC_6H_5\\ >O\\ CO\end{matrix}\right.$ because on treating the acid chloride with benzene and aluminium chloride it gave diphenylphthalide.

Graebe and Ullman[2] have shown that, if, in the preparation of the acid chloride, temperatures above 100° are used, the product is anthraquinone. This would indicate the formula $C_6H_5—CO—C_6H_4—COCl$, and the preparation of the amide and the change of the latter to aminobenzophenone is in accordance with the latter formula. Haller and Guyot also prepared the methyl ester of *o*-benzoyl-benzoic acid in five different ways, including the action of the acid chloride on methyl alcohol, and in each case obtained the ester first described by Plascuda[3] (m. p. 51–52°).

Meyer[4] prepared the acid chloride of *o*-benzoyl-benzoic acid by dissolving the acid in thionyl chloride and removing the excess of thionyl chloride in a current of dry air at 50°. He obtained a colorless syrup which would not crystallize but which, when added to methyl alcohol, gave an ester having the melting point 80–81°. Meyer obtained the same ester from the acid chloride prepared by the action of phosphorus trichloride on the acid. He tried in various ways to convert this ester into the ester having the melting point 51–52° but always failed, and he concluded that the acid chloride prepared by the thionyl chloride method or by the phosphorus trichloride method is the isomeric form of that obtained by the use of phosphorus pentachloride.

The author prepared *o*-benzoyl-benzoyl chloride using the method employed by Haller and Guyot. 22.6 g. of the anhydrous acid were suspended in 300 g. of carbon disulfide and 20.8 g. of phosphorus pentachloride added in small portions. After the evolution of hydrogen chloride had ceased the carbon disulfide and phosphorus oxychloride were distilled off under reduced pressure, the temperature being kept below 100°. The thick heavy oil was dissolved in anhydrous ether and the solution, allowed to evaporate slowly over sulfuric acid, gave large colorless crystals, m. p. 59–60°. Several attempts to crystallize the oil by

---

[1] *Bull. soc. chim.*, [3] **25**, 54 (1901).

[2] *Ann.*, **291**, 10 (1896).

[3] *Ber.*, **7**, 987 (1874).

[4] *Monatsh.*, **25**, 475 (1904).

dissolving in benzene and adding ligroin proved fruitless, although this is the method described by Haller and Guyot.

The acid chloride was also prepared by Meyer's method. 15 g. of the anhydrous acid were dissolved in about 15 cc. of pure, almost colorless thionyl chloride. A current of dry air was then passed through the flask which was heated to about 50° and after a few hours the contents of the flask solidified. This was recrystallized from ether and gave crystals, m. p. 59–60°, identical with those obtained by the other method.

Through the kindness of Prof. T. L. Walker, a microscopic examination of these crystals was obtained. They are doubly refracting and biaxial, their commonest section is a rhomb and they extinguish parallel to the diagonals of the rhomb, indicating a crystal of the rhombic, monoclinic or triclinic system.

As the acid chloride is extremely easily affected by the moisture of the air, it was difficult to get a good specimen for analysis and the chlorine content came low.

Calc. for $C_{14}H_9O_2Cl$: Cl, 14.5. Found: Cl, 13.6.

Preparation of the Cyanide.—Three methods were used in the attempt to prepare *o*-benzoyl-benzoyl cyanide.

1. The acid chloride and mercuric cyanide were dissolved in anhydrous acetone and heated on the water bath for several hours.

2. The acid chloride and anhydrous hydrogen cyanide were dissolved in anhydrous ether and pyridine added.

3. The acid chloride and mercuric cyanide were heated in a sealed tube.

The third method was the only one which yielded any cyanide and it was also unsuccessful when potassium cyanide was substituted for the mercuric salt. About 10 g. of the acid chloride prepared by the thionyl chloride method was mixed with an excess of finely ground mercuric cyanide and heated 8–9 hours in a sealed tube at 155–165°. Great care must be taken to prevent exposure of the chloride to air and temperatures higher than 165° decrease the yield. The contents of the tube were treated with alcohol and filtered. On adding water to the alcohol solution it turned milky and, on standing, white crystals separated out which were further purified by redissolving in alcohol and adding water. Yield about 65%.

Calc. for $C_6H_5.CO.C_6H_4.CO.CN$: N, 5.97. Found: N, 6.09, 5.97, 5.99.

The cyanide melts at 70°, and is very soluble in acetone, ether, benzene, toluene, acetic acid and ethyl acetate; less soluble in alcohol and ligroin and insoluble in water.

This preparation was repeated, using 10 g. of the chloride prepared by the use of phosphorus pentachloride. The yield was about 50% and the cyanide was identical with that obtained in the first preparation.

Summary.

1. *o*-Benzoyl-benzoyl chloride has been prepared by the action of phosphorus pentachloride on the acid. Its m. p. is 59–60° while that obtained by previous investigators melted about 70°. Possibly their chloride had been affected by moisture.

2. *o*-Benzoyl-benzoyl chloride has also been prepared by the action of thionyl chloride on the acid. It is identical with the product obtained by the previous method. It had previously been described as a thick oil which would not solidify and was thought by Meyer to be an isomer of the other.

3. *o*-Benzoyl-benzoyl cyanide has been prepared by the action of mercuric cyanide on the acid chloride obtained by each of these methods. The same product is obtained.

4. The experiments described give no evidence of a necessity for tautomeric formulas for *o*-benzoyl-benzoic acid.

The preparation of the esters is being repeated in this laboratory and the results will be published very shortly.

These experiments were carried out under the direction of Professor F. B. Allan.

UNIVERSITY OF TORONTO.

CORRECTION.

On page 391 of the February issue read "*p*-nitrophenylhydrazone" and "*p*-nitrophenylhydrazine" instead of "*p*-nitrophenylsemicarbazone" and "*p*-nitrophenylsemicarbazine."

NEW BOOKS.

Elements of Physical Chemistry. By HARRY C. JONES, Professor of Physical Chemistry in the Johns Hopkins University. Fourth edition, revised and enlarged. New York: The Macmillan Company, 1915. Pp. xiv + 672. Price, $4.00.

With a comparative page increase of about 20%, this fourth edition retains most of the characteristics of the first edition of the work, which appeared in 1902. "Considerable new matter has been incorporated in the fourth edition of this work. Since the book is now large enough for the purpose which it was meant to fulfill, this has been done in the smallest space possible. The new material has, for the most part, been inserted at the ends of the several chapters, to avoid, as far as possible, destroying the plates." This quotation from the author's preface points to a conservatism which embraces general viewpoint as well as choice, arrangement and treatment of subject matter. The style is pleasing, the literature references are copious and the mechanical production of the book is excellent. ALAN W. C. MENZIES.