The following specific rotations of the pure tetracetate in different solvents were found, using a 2 dcm. tube: in chloroform[1] solution $[\alpha]_D^{20} =$ —17.8 (4.7 g. per 100 cc.), in benzene —23.4 (3.5 g. per 100 cc.), in 99.5% glacial acetic acid —11.0 (4.1 g. per 100 cc.), in ethyl alcohol —6.2 (4.4 g. per 100 cc.), and in water —12.9 (4.4 g. per 100 cc.). The substance shows mutarotation. Thus the specific rotation in chloroform gradually changed at room temperature from its initial value —17.8 to —6.9 in one day, —3.1 in six days, and —1.9 in three months. An aqueous solution changed in specific rotation from —12.9 to +21 in four months.

Fehling's solution is readily reduced by the tetracetate. The melting point of the pure substance is 71–73° (corr.).

By the acetylation of 1 g. of the tetracetate with acetic anhydride and sodium acetate 0.6 g. of the crystalline third pentacetate of galactose was obtained, which was identified by its melting point and specific rotation. This conversion proves that the ring in the pentacetate structure is not changed during the transformation through the bromoacetyl compound to the tetracetate. Since the tetracetate shows mutarotation towards increasing dextrorotation, it is to be regarded as the beta form.

A crystalline phenylhydrazone of the new tetracetate was prepared through the interaction of seven g. of the tetracetate and 5 cc. phenyl hydrazine in ether solution. Two estimations of nitrogen in the crystals gave 6.68 and 6.61%, in comparison with the theoretical value of 6.41% for a tetracetyl galactose phenylhydrazone. The substance melted at 95° and showed a specific dextrorotation of +15.5 in chloroform.

WASHINGTON, D. C.

THE METHYL ESTER OF ORTHOBENZOYL-BENZOIC ACID.

By T. C. McMullen.

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Plascuda[2] described the methyl ester of *o*-benzoyl-benzoic acid and Haller and Guyot,[3] later, prepared it in five different ways, one of which was by the action of methyl alcohol on the acid chloride prepared from phosphorous pentachloride. In each case they obtained the same ester as described by Plascuda (m. p. 51–52°).

Meyer[4] prepared the ester by the action of methyl alcohol on the acid chloride. The acid chloride was prepared in three ways: By (*a*) thionyl chloride, (*b*) phosphorus pentachloride, and (*c*) phosphorous trichloride. In the second case he obtained the ester already described, but in the other

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[1] *Chloroformum purificatum*, U. S. P.

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

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

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

two experiments he obtained an isomeric ester whose melting point was about 80°. He inferred that the acid chloride in (*a*) and (*c*) is an isomer of that in (*b*).

As Martin[1] has shown that the acid chloride prepared by thionyl chloride is identical with that prepared by phosphorus pentachloride, it seemed worth while to repeat Meyer's preparation of the esters.

In each case the acid chloride was prepared as described by Meyer, and was usually obtained in the crystalline form. It was then added to excess of methyl alcohol in which it dissolved with evolution of hydrogen chloride. After about half an hour the solution was poured into dilute sodium bicarbonate solution and an oil separated which solidified after standing for some hours. It was found that the oil solidified sooner if it were not extracted with chloroform as recommended by Meyer. The solid was recrystallized by dissolving in methyl alcohol and adding water till the precipitate began to appear.

Experiment 1.—The acid chloride was prepared by using thionyl chloride and obtained in the crystalline form as described by Martin. The yield of ester was about 90%; m. p. 51.5°.

Calc. for $C_{15}H_{12}O_3.CH_3O$: 12.9. Found: 12.7, 12.8.

As Meyer obtained some of the low melting ester when he removed the thionyl chloride as completely as possible, but prevented this by using the acid chloride in presence of thionyl chloride, this experiment was repeated using the solution of the acid chloride in the thionyl chloride but the same product was obtained with no trace of Meyer's ester.

Experiment 2.—The acid chloride was prepared from phosphorus pentachloride and used in the crystalline form. The ester melted at 51.7°.

Experiment 3.—The acid chloride was prepared from phosphorus trichloride and, as it was not entirely freed from phosphorus trichloride and phosphorous acid, was not in the solid form. The ester was identical with that obtained in the two previous cases.

In each of the three preparations the product was subjected to fractional crystallization and no trace of another ester was found except in one instance where the acid chloride had been dissolved in ether. This product contained some ethyl ester melting at 58°.

Summary.

1. Meyer's preparation of the methyl ester of *o*-benzoyl-benzoic acid has been repeated using the acid chloride prepared in three different ways as described by him. No trace of the ester with the higher melting point was found.

2. Martin's conclusion that the *o*-benzoyl-benzoyl chloride prepared

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[1] THIS JOURNAL, 38, 1142 (1916).

from thionyl chloride is the same as that prepared from phosphorus pentachloride is confirmed, and it is shown that the acid chloride prepared from phosphorus trichloride is identical with the others since it gives the same methyl ester.

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

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[CONTRIBUTION FROM THE CHEMICAL DEPARTMENT OF THE HAWAII AGRICULTURAL EXPERIMENT STATION.]

ON THE DETERMINATION OF SMALL QUANTITIES OF HYDROCYANIC ACID.

BY MAXWELL O. JOHNSON.

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In connection with some recent chemical work on cassava, there developed a need for a rapid and accurate method for the determination of small quantities of hydrocyanic acid. The silver gravimetric method is not suitable for small amounts of cyanides, such as one milligram, and the reducing substances found in plant distillates interfere with this and the various titration methods. These reducing substances also interfere with the picric acid colorimetric method of Waller[1] as shown by Chapman.[2]

Moore[3] determines the hydrocyanic acid in cassava by heating 540 grams of pulped root in an iron retort for two hours, absorbing in potassium hydroxide solution the hydrocyanic acid distilled. The distillate is acidified with sulfuric acid and redistilled into water containing 5 cc. of tenth-normal potassium hydroxide. As the distillation proceeds, the distillate is titrated with tenth-normal silver nitrate and potassium hydroxide added as necessary, to provide for a minimum excess of potassium hydroxide present when the titration is completed. The method appears accurate but requires special iron retorts and a long distillation. The writer found when cassava was distilled into potassium hydroxide solution, that organic matter passing over colored the distillate yellow or orange. On adding an excess of sulfuric acid and redistilling into potassium hydroxide solution, organic matter again passed over. This interfered with the silver nitrate titration.

Various studies have been made of the Prussian blue colorimetric method, by Berl and Delpy[4] by Lander and Walden,[5] by Vorländer,[6] by Knight,[7]

[1] *Proc. Roy. Soc.* (*B*), **82,** 574 (1910).

[2] *The Analyst,* **35,** 471 (1910); **36,** 269 (1911).

[3] Cassava, U. S. Bur. Chem., *Bull.* **106,** 12.

[4] *Ber.,* **43,** 1430 (1910).

[5] *The Analyst,* **36,** 266 (1911).

[6] *Ber.,* **36,** 181 (1913).

[7] *J. Ind. Eng. Chem.,* **6,** 909 (1914).