and evaporated to dryness. No change in weight and scarcely any in color resulted after two such treatments. This behavior toward water is surprising, for from the published descriptions of zirconium tetrachloride and tetrabromide, it was to be expected that the iodide would prove to be a hygroscopic compound easily decomposed by water. It seems, however, to more nearly resemble the fluoride which Deville states to be a colorless crystalline substance volatile at a white heat and insoluble in water or acids.

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PHTHALIMID.[1]

BY J. A. MATHEWS.

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A NUMBER of years ago Prof. C. E. Colby and Mr. Dodge, of Columbia University were led to try the effect produced by heating together, under pressure, mixtures of (1) fatty acids and fatty nitrils; (2) fatty acids and aromatic nitrils; (3) fatty nitrils and aromatic acids; and (4) aromatic acids and aromatic nitrils. The reactions were carried on in sealed tubes. The score or more reactions that they tried were done at temperatures ranging from 235° to 280° C. As the result of their work they reached these conclusions regarding what is likely to take place, at least when monobasic acids and mononitrils are employed.[2]

1. Fatty nitrils and fatty acids give secondary amids.

2. Fatty nitrils and aromatic acids give fatty acids and aromatic nitrils.

3. Aromatic nitrils and fatty acids give mixed secondary amids.

4. Aromatic nitrils and aromatic acids gave secondary amids, except in one case when exceptionally high heat was used (280°) in which case the cyanide of the higher radicle was formed.

In regard to dibasic acids and dicyanides not so much has been done. Miller first tried reactions with succinic acid and ethylene cyanide.[3] He found that succinimid resulted from each of the following experiments:

[1] Read before the American Chemical Society. New York Section, June, 1896.

[2] *Am. Chem. J.*, 13, *1891*.

[3] This Journal, 16, 443, *1894*.

1. Ethylene cyanide and acetic acid heated in a sealed tube.
2. Acetonitril and succinic acid, and
3. Ethylene cyanide and succinic acid.

Some other acids in this series have been tried. Malonic acid was rather imperfectly tested. In every case the tubes exploded and malonimide was not obtained at all.

Seldner[1] reports parallel results to those obtained by Miller when he used glutaric acid and trimethylene cyanide. In the following trials which he made glutarimid resulted every time:

1. Glutaric acid (1 mol.) and acetonitril (2 mols.).
2. Glutaric nitril (1 mol.) and acetic acid (2 mols.).
3. Glutaric acid and glutaric nitril, equal molecules.

Until the writer, at Prof. Colby's suggestion, made the experiments hereinafter recorded no one, to my knowledge, had applied these methods to aromatic, dibasic acids. The results of the first experiments are very gratifying and I hope in the near future to try the reaction with other dibasic, aromatic acids.

Since no information regarding phthalic nitril could be obtained I was obliged to do without it. The experiments were therefore made with phthalic acid and propionitril.

Four sealed glass tubes each containing phthalic acid (1 mol.) and propionitril (2 mols.), plus about three drops of acetic anhydride were heated in an oven for various lengths of time and at different temperatures.

Tube I. The first tube was opened after ten hours heating at 180° C. The contents of the tube had a pungent acid odor and were treated with cold dilute potassium carbonate solution. A residue consisting of needle-like crystals remained. These were filtered off, washed with water, and dried. The crystals then had a melting point of 228° C. I immediately suspected from this melting point that phthalimid had been formed by the reaction

$$C_6H_4(COOH)_2 + C_2H_5CN = C_6H_4(CO)_2NH + C_2H_5COOH.$$

The yield of phthalimid in this experiment was about sixty per cent. of the theoretical.

[1] *Am. Chem. J.*, 17, *1895*.

Tube II. On heating the remaining three tubes higher No. 2 broke at about 215°.

Tube III. After further heating of eight hours at 200° to 215° C. the third tube was opened and the contents treated with potassium carbonate solution. The crystals remaining were not so light colored as those from Tube I, and were so different in appearance that it was thought some other reaction had taken place. The melting-point, however, was about the same as in the first case, *viz.*, 227°. Yield eighty-four per cent.

Tube IV. Exploded at 258° C.

Since the theoretical equation requires only one molecule of nitril to one of phthalic acid two more tubes were prepared, each containing equal molecules of phthalic acid and propionitril.

Tube V. After three and a half hours at 180°–200° C. the fifth tube was opened and treated with potassium carbonate solution as before. Residue crystalline; melting-point 228.5°, yield eighty-eight per cent.

Tube VI. Heated five and a half hours at 180°–200°, melting point of residue, insoluble in cold, dilute potassium carbonate solution, 228.3° C., yield 92.5 per cent.

The crystals of phthalimid were all more or less colored, the color being darkest in the case of the third tube which had been subjected to long, high heat. In no instance was any outward pressure noticed on opening the tubes.

Portions of the products were recrystallized from acetic acid, from alcohol, and from alcohol with the addition of animal charcoal to decolorize. The melting points of the recrystallized products were a little higher than before purification, *viz.*, 230°, 229.5° and 229.5°, respectively. These agree very closely with the point given in Beilstein.

Biedermann[1] gives the melting-point as 228° or 229° C.

Michael[2] gives the corrected melting-point as 233.5° C. The decolorized crystals from alcohol form beautiful long needles.

Notwithstanding the close agreement of the melting-points obtained with those given by the authorities, some other tests were made to show that the product was nothing else than

[1] *Ber. d. chem. Ges.*, 10, 1166.

[2] *Ber. d. chem. Ges.*, 10, 579.

phthalimid. A portion of the crystals heated with potassium hydroxide went into solution with evolution of ammonia. Another portion of the crystals were covered with concentrated ammonia and allowed to stand for some time. They were soon converted into microscopic crystals of phthalamid

$$(=C_6H_4(CONH_2)_2).$$

These crystals were filtered off, washed, and dried. They melted at 217.5° (uncorrected) with an evolution of ammonia, which began at about 200°. The phthalamid was further proved by its insolubility in cold water, alcohol, and ether, and by boiling it with water it was decomposed, giving off ammonia and on cooling phthalimid, melting at 230° C., crystallized out.

The results of these tests show conclusively that the product is phthalimid and that when it is made by the action of equal molecules of acid and nitril the yield is large. The reaction works comparatively readily, and at a much lower temperature than was needed to affect the reactions recorded by Colby and Dodge. It is highly probable that with slight changes of conditions any one of a variety of nitrils would give the same result. I hope to report further experiments with phthalic acid and other dibasic aromatic acids at a later day.

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DETERMINATION OF SULPHURIC ACID.

BY N. J. LANE.

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SOME months ago, before hearing of the controversy between Dr. Lunge and Mr. Gladding, some experiments were made on this subject, the results of which sustain Mr. Gladding's case. The determinations were made on nearly normal sulphuric acid to establish its strength with the following results:

	Barium chloride added suddenly.	Barium chloride added by drops.
1. Sulphuric acid	50.03	49.23
2. " "	49.90	49.32
3. " "	50.14	....

And the average of several practically identical titrations on C. P. sodium carbonate gave sulphuric acid 49.33.

The above results were obtained with the greatest care, and every precaution used to insure accuracy. This, in my opinion, conclusively proves the accuracy of Mr. Gladding's statements.