The bright yellow compound obtained by Bishop Tingle and Blanck[1] by the action of a mixture of nitric and oxalic acids on picranilide (Exp. 96) after recrystallization from alcohol is deposited as a bright yellow, granular powder, melting at 197–200°. Found, C 41.29, H 2.01, N 19.88. Calculated, C 41.26, H 2.00, N 20.05. These results indicate that the compound is a picronitranilide (tetranitrodiphenylamine), $O_2NC_6H_4NHC_6H_2(NO_2)_3$.

By the action of a mixture of nitric and trichloracetic acids on picranilide, Bishop Tingle and Blanck[1] obtained a yellow substance (Exp. 95). After recrystallization from glacial acetic acid it melts sharply at 200°. When recrystallized again from the same solvent the melting point was 213°. Found, C 40.47, H 2.09. This substance is evidently a tetranitrodiphenylamine, but we are unable to state positively whether it is isomeric or identical with the preceding compound.

Another *tetranitrodiphenylamine* is prepared according to the method of Bishop Tingle and Blanck[2] by dissolving diphenylamine in concentrated nitric acid and pouring the solution into cold water. The crude product melts at 190–194°. After recrystallization from nitrobenzene it melts at 200°. When boiled with glacial acetic acid only a small portion dissolves, the residue melts at 275° and analysis shows it to be a *tetranitro derivative*. Found, C 41.40, H 1.84, N 19.57. Calculated, C 41.26, H 2.00, N 20.05. We made numerous attempts to hydrolyze the compound but they were unsuccessful. The substance is easily reduced by tin and hydrochloric acid; the product is extremely readily soluble and is quickly oxidized by air. Hitherto we have been unable to obtain any crystalline derivatives from this reduction product.

The investigation is being continued in this laboratory.

Summary.

1. We have investigated the interaction, under varied experimental conditions, of the three isomeric nitranilines with formic, acetic, stearic, oxalic, succinic, tartaric, citric, benzoic, salicylic, phthalic and picric acids.

2. The nitration products of the anilides of most of the above acids, and also the nitration products of propanilide and diphenylamine, which were prepared by Bishop Tingle and Blanck, have been examined in detail and their constitution has been determined.

3. A considerable number of new compounds have been prepared. The work will be continued in this laboratory during the coming academic year.

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THE ANHYDRIDES OF ISOPHTHALIC AND TEREPHTHALIC ACIDS.

BY JOHN E. BUCHER AND W. CLIFTON SLADE.[3]

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The anhydride of ortho-phthalic acid is obtained very easily by means of the usual methods for the preparation of anhydrides. It is also obtained by simply heating the acid. No anhydrides of the isomeric meta-

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[1] *Loc. cit.*, p. 1411.

[2] *Ibid.*, p. 1405.

[3] Read at the New Haven meeting of the Am. Chem. Soc., July, 1908.

and para-acids are known, and many statements that these two acids do not or cannot form anhydrides have been made. Perkin and Kipping[1] state that "phthalic acid, like succinic acid, is converted into its anhydride when strongly heated, but it is very important to notice that an anhydride of isophthalic acid or terephthalic acid cannot be produced; it is, in fact, a general rule that the formation of an anhydride from *one* molecule of the acid takes place only when the two carboxyl-groups in the benzene nucleus are in the *o*-position, never when they occupy the *m*- or *p*-position." Also, Richter[2] states: "Again, *o*-phthalic acid is distinguished from the *m*- and *p*-bodies by its ability to form an anhydride and other cyclic derivatives," and in another place he states that isophthalic acid does not form an anhydride.

Some facts noticed in this laboratory lead to the conclusion that isophthalic and terephthalic acids,[3] under some conditions, might form anhydrides. In fact, the anhydrides were obtained by simply dissolving the acids in acetic anhydride and then distilling off the liquid at 200°. This shows that it is practically just as easy to prepare anhydrides from the meta- and para-acids as from the ortho-acid and that statements like those quoted above need modification or, at least, some qualification. The statement that meta- or para-acids do not form anhydrides must be abandoned. The statement that they do not form inner anhydrides may still be true as it is probable that our anhydrides have a higher molecular weight and a different constitution. If we state that, *upon heating*, only the ortho-acid forms an anhydride while the others do not, we have a practicable method not only of distinguishing the ortho-acid but also of separating it from the other two by subsequent treatment with sodium carbonate solution. That this is a very general method of separating aromatic ortho-dicarboxylic acids from other acids is shown by the work of many investigators. It can also be applied in many cases to determine the presence of pairs of ortho-carboxyl groups in aromatic tetra- or hexa-carboxylic acids unless the constitution is such as to make ambiguous results possible. The 1–2–3–4–benzene tetracarboxylic acid[4] is an example of the latter class because we may consider it to contain either two pairs of ortho-groups (1–2 and 3–4) or one pair (2–3) of ortho-groups and one pair (1–4) of para-groups. On heating, it reacts in the latter sense, yielding only the partial anhydride.[4]

Experimental.—The following directions were found to be very satisfactory for the preparation of isophthalic anhydride. Twenty-five grams of finely powdered isophthalic acid were heated with 150 cc. of carefully distilled acetic anhydride in a 500 cc. distilling bulb. As soon as all of the acid had dissolved, the excess of acetic an-

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[1] Organic Chemistry (Philadelphia, 1908), p. 437.

[2] Organic Chemistry (Philadelphia, 1900), pp. 239 and 242.

[3] THIS JOURNAL, 30, 1263 (1908).

[4] Jacobsen, *Ber.*, 17, 2518 (1884).

hydride was distilled off at 200° in the oil-bath. The viscous product thus obtained was finally heated to the same temperature at 10 to 15 mm. pressure, using a phosphorus pentoxide tube to exclude water vapor. The heating was usually continued for an hour, the flask being moved so that the product formed a thin layer, thus facilitating the removal of volatile material. In this way, a granular substance is formed. It can be removed from the flask by means of a wire. Mixed anhydrides are first formed and these constitute the oil which is obtained when the greater portion of the reagent is distilled off. These are then decomposed in the final heating—leaving the isophthalic anhydride.

When the anhydride, thus prepared, is ground with sodium carbonate solution for several minutes, so little passes into solution that the alkaline liquid only gives a slight turbidity when it is acidified. If the ground solid is then allowed to dry and again treated with sodium carbonate, more will pass into solution. This indicates hydrolysis and shows that it is advisable to exclude water in working with the substance. It dissolves readily in caustic alkali solutions upon warming. These solutions, upon acidifying, yield a precipitate of pure isophthalic acid and they contain no acetic acid, thus showing the absence of mixed anhydrides. The anhydride is practically insoluble in the ordinary neutral organic solvents. It is also very non-volatile. These properties prevented a determination of its molecular weight. It decomposed on heating, without showing a sharp melting point.

A portion of the finely powdered isophthalic anhydride was prepared for analysis by heating to 183° at a pressure of less than 1 mm. for several hours. At first there was slight loss in weight, a trace of sublimate, soluble in sodium carbonate, being obtained. After some time, the weight became constant.

Analysis:

Calculated for $C_6H_4(CO)_2O$: C, 64.86; H, 2.70; for $C_6H_4(CO.O.COCH_3)_2$: C, 57.60; H, 4.00.

Found: C, 64.47, 64.57; H, 2.94, 2.95.

The anhydride of terephthalic acid was prepared in nearly the same way as that of the meta-acid. In this case, it was necessary to use much more acetic anhydride (90 cc. per gram of acid) in dissolving the acid. The final heating was again 200°. In this case, the products separated in the crystalline form at the close of the distillation.

This anhydride resembles the meta-compound closely in its general properties. It is not soluble in sodium carbonate but dissolves in sodium hydroxide on warming. The terephthalic acid can be recovered from this alkaline solution by acidifying. It is non-volatile and is not soluble in the ordinary neutral organic solvents. It decomposes when heated.

Owing probably to the difference in solubility, it is not so easy to obtain pure as the meta-anhydride. This is shown by the analysis which gave 63.6 per cent. of carbon. We were unable to prepare another specimen for analysis on account of lack of time, but there is no reason to doubt the possibility of getting a pure substance. Possibly the temperature of 200° is rather too high for the final heating in the preparation of these anhydrides.

The properties of these anhydrides indicate that they have a high molecular weight and that they may be represented by the formula $[C_6H_4(CO)_2O]_x$. A further investigation of these substances as well as of their substitution products will be undertaken in this laboratory.

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