NOTES.

Note on the Mononitro-o-Phthalic Acids.—Since the publication in this Journal of the article by Bogert and Boroschek[1] upon the mononitro-*o*-phthalic acids, certain facts have come to light which seem to call for a few additional notes from us.

In the first place, we have discovered, among a number of dissertations recently secured by Columbia University, several dealing wholly or in part with the nitrophthalic acids. Two of these, namely, one by Max Levi, submitted to Freiberg (i. B.) University in 1891, the other by Adolph Koch, submitted to the University of Geissen in 1900, antedated part of the work reported by us. So far as we know these results have not been published in any of the chemical journals and do not appear in "Beilstein." Of the derivatives prepared by us, the following are also described in these dissertations.

3-Nitrophthal-1-Amic Acid.—By the action of hydrochloric acid upon the sodium salt of the imide, Levi[2] obtained a crystalline compound to which he assigned the 1-amic acid structure. The acid prepared by us by the action of baryta water upon the imide, and for which we suggested the 2-amic acid constitution, has recently been shown by Kahn[3] to be the 1-amic acid. As Levi did not analyze his product and gives very few data concerning it, it is doubtful whether he really had the pure 1-amic acid in hand, particularly as he reports the substance to be "quite easily" soluble in ether, whereas the 1-amic acid is really very difficultly soluble in ether.

3-Nitrophthal-1-Anilic Acid.—Levi also reports an anilic acid, crystallizing in white needles, melting-point 232°, which does not at all correspond to the pale yellow needles obtained by us, which melt at 180° with formation of the anil. We thought it likely that this acid had the 2-anilic acid form, but Kahn's work makes it seem much more likely that it possesses the 1-anilic acid structure.

3-Nitrophthalamide.—The amide prepared by Levi melted at 219°, while our product melts at 200°-201° with formation of the imide.

4-Nitrophthalanilic Acid.—The anilic acid prepared by Levi

---

[1] This Journal. **23**, 740-761 (1901).

[2] *Loc. cit.*

[3] *Ber. d. chem. Ges.*, **35**, 3866 (1902).

melted at 204° (uncorr.); our product at 181° with formation of the anil.

4-Nitrophthalimide.—This was prepared by Levi by the action of ammonia upon the anhydride and also by the action of ammonium thiocyanate upon the free acid. His product is apparently the same as that obtained by us subsequently. To the imides of both nitrophthalic acids, Levi assigns the unsymmetrical structure, in the derivatives of the 3-nitro acid placing the imide group (:NH) upon the carbon non-adjacent to the nitro group (a formula, by the way, recently supported by Kahn, in a private communication to one of us).

4-Nitrophthalanil.—Prepared by Levi before either Graebe and Buenzod[1] or ourselves.

4-Nitrophthalamide.—Also prepared by Levi before us.

4-Azophthalic Acid.—Koch[2] obtained an azo acid by the electrolytic reduction of 4-nitrophthalic acid in alkaline solution, and describes the substance as an orange-yellow to rose-red precipitate, decomposing and partly subliming at 200°. We reported two different forms of 4-azophthalic acid: one, by reducing an alkaline solution of 4-nitrophthalic acid with sodium amalgam, was a salmon-colored, crystalline substance not melting below 360°, and giving a silver salt insoluble in hot water; the other, by oxidizing azophthalide with alkaline permanganate solution, separated as a reddish yellow, crystalline precipitate, melting with decomposition at 285°-300°, and yielding a silver salt partly soluble in hot water. The products of all these methods show about the same solubilities in water, alcohol and ether.

It seems not amiss in this connection also to call attention to the fact that 3-nitrophthalic anhydride was prepared by Leupold[3] from the corresponding acid and acetyl chloride three years before Lipschitz[4] reported the same method for the production of the anhydride.

Kahn has recently criticized our method of preparing this anhydride, stating that, in his experience, six to eight hours' heating of the acid at 235°-240° causes considerable decomposition. In his first article[5] he recommends a temperature below 218°, while

---

[1] *Ber. d. chem. Ges.*, **32**, 1992 (1899).

[2] *Loc. cit.*

[3] Inaugural Dissertation, Basel, 1897, p. 22.

[4] *Monatsh. Chem.*, **21**, 793 (1900).

[5] *Ber. d. chem. Ges.*, **35**, 472 (1902).

in his second[1] he states that a temperature of 230° is about right. As the temperature reported by us (235°-240°) merely represented the temperature of the heating medium, the reaction being conducted in an open flask in the oil-bath, it is probable that the actual temperature of the melt was not far from 230°. We did not determine the temperature of the melt exactly, since our interest lay more in determining the possibility of obtaining the anhydride by heating the acid than in the question of the exact temperature at which the best yield was secured, in view of the fact that Lipschitz[2] shortly before had reported that the anhydride could not be satisfactorily prepared in this way. The fact that the acid is liable to decompose when heated too high was, of course, observed by the earliest workers in this field.[3] Our product, however, was not overheated and showed no signs of decomposition, the solidified melt being light yellow, crystalline and homogeneous. The duration of the reaction, as reported by us (six to eight hours) represented the time consumed in raising the temperature of the oil-bath very gradually until it reached 235°-240°, when no more water was evolved and the flask was removed from the bath. As Kahn has shown, heating for half an hour at 230° is sufficient to complete the reaction.

Concerning the discovery of 3-nitrophthalic acid, the impression might be gathered from certain reference works (Beilstein, Roscoe-Schorlemmer, *et. al.,* in which the name of Marignac precedes that of Laurent, in giving the earliest literature upon the subject, that the work of the former anticipated that of the latter. As a matter of fact, Laurent's work antedated Marignac's by at least a year, as appears from the following: Laurent, in studying the action of nitric acid upon naphthalene, isolated, among other products, an acid which he called "nitrophthalic," and prepared its anhydride, acid ammonium salt and imide. These results were sent to the French Academy of Sciences, on March 16, 1840.[4] By a strange mischance, not only this memoir but four others by the same author upon new compounds of naphthalene were mislaid in the office of the latter journal and lost. When Laurent learned of this loss, he immediately requested De Quesneville to

---

[1] *Ber. d. chem. Ges.*, **35**, 3859 (1902).

Loc. cit.

[3] Laurent: *Compt. rend.*, **12**, 1193; Marignac: *Ann. Chem.* (Liebig), **38**, 9; Laurent: *Rev. scientif. Indus.*, **6**, 95 and **13**, 602; de Aguiar: *Ber. d. chem. Ges.*, **5**, 899; Kronberg: Inaugural Dissertation, Göttingen, 1881, p. 32, etc.

[4] *Rev. scientif. Indus.*, **5**, 363; **6**, 76-77.

copy the duplicates which had been deposited with the secretary of the Academy and to publish the same in the *Revue scientifique et Industrielle.* This was done, the article appearing four or five months later in Vol. 6, pp. 76-99. Laurent also reported his work upon nitrophthalic acid at the meeting of the Academy, June 21, 1841.[1] Before the publication of Laurent's delayed article in the *Revue scientifique et Industrielle,* a paper appeared in Liebig's *Annalen* (38, 1-13) by Marignac of Geneva, likewise dealing with the action of nitric acid upon naphthalene and announcing the discovery of "nitronaphthalic acid" (identical with Laurent's "nitrophthalic acid") and the preparation of some of its salts. Later in the same year (1841), Laurent[2] called attention to the fact that his work had anticipated Marignac's by at least a year.[3] and so far as we are aware, this claim was never disputed by Marignac. It seems, therefore, that the major portion of the credit for the discovery of nitrophthalic acid belongs to Laurent, not alone because he was actually the first to obtain the acid, but also because Marignac (as he himself acknowledges—*Loc. cit.*) was only following in a line of investigation already largely worked out by Laurent. M. T. BOGERT AND L. BOROSCHEK.

ORGANIC LABORATORY, COLUMBIA UNIVERSITY,
May 14, 1903.

A Cheap and Efficient Water-blast.—The work performed in the chemical laboratory of Cornell College emphasized the necessity of a water-blast, and some of the well-known kinds were purchased. The laboratory is situated on the third floor of the building where the water pressure was found to be scarcely 30 pounds to the square inch. This was not sufficient to maintain the blasts satisfactorily. It was therefore necessary to set about to devise a blast which would be suitable where the water pressure is low and which would give good results with a small jet of water. The apparatus here described has been in use for about four months and seems fully to meet the conditions.

Experiments with various devices were made, but the one that has given the most satisfactory results consists of a small water-wheel (1), a large pulley-wheel (2) connected by belt with a small one (3) for driving a fan wheel (4), all of which are enclosed in a rectangular wooden box 7x12x24 inches.

---

[1] *Compt. rend.*, **12**, 1193.
[2] *Rev. scientif. Indus.*, **9**, 31.
[3] *Ibid.*, **5**, 363-364.