colored mass had settled out of the chloroform. By the fractional crystallization of its aqueous solution as previously described, the higher hydrate of the ethyl ester of gallotannic acid was obtained. This gave all the reagent tests for tannin, for glucose, and ethoxyl groups. It melted at 132°. The maximum yield I obtained was only about 5% of the theoretical.

Summary.

1. Two crystalline derivatives of tannin have been obtained. They are ethyl esters of gallotannic acid differing in the amount of water of crystallization. The previous analyses of gallotannic acid varied because crystalline derivatives were not known and therefore pure material was very difficult to obtain.

2. These esters were synthesized from alcohol and gallotannic acid and one of them was also synthesized from ethyl gallate and glucose.

3. Various analyses show that the formulas for these esters are $C_{41}H_{27}O_{21}(OC_2H_5)_5 \cdot 5H_2O$ and $C_{41}H_{27}O_{21}(OC_2H_5)_5 \cdot 15H_2O$, and that they are glucosides of gallic acid in which one formula weight of glucose and five formula weights of gallic acid are represented in one formula weight of the ester. This gives the formula $C_{41}H_{32}O_{26}$ for gallotannic acid.

4. Dissociation of the hydrated ester into water and anhydrous ester would account for the low formula-weight determinations in acetone, etc.

This work was done under the direction of Professor W. Lash Miller.

UNIVERSITY OF TORONTO.

ACTION OF AMINES ON PHTHALIC ACID. VII.[1]

BY J. BISHOP TINGLE AND S. J. BATES.

The work described in the earlier papers by the senior author and his colleagues has shown that the phthalamidic acids combine with amines to form salts, $RNHCOC_6H_4CO_2NH_3R'$. Secondary or tertiary amines, if they are not too negative, convert these salts into imides, $C_6H_4 {<}{\overset{CO}{\underset{CO}{}}}{>}NR$ or $C_6H_4 {<}{\overset{CO}{\underset{CO}{}}}{>}NR'$, whereas primary amines give rise to one or more of the following products: the amidic acid $R'NHCO$ $C_6H_4CO_2H$, the amides $RNHCOC_6H_4CONHR$ or $C_6H_4(CONHR')_2$, and the imides formulated above. In the case of the secondary phthalamidic acids, $RNR'COC_6H_4CO_2H$, where R and R' may represent similar or dissimilar groups, the amine $R''NH_2$ behaves somewhat differently; it may cause hydrolysis of the original amidic acid to phthalic acid, or

[1] The previous papers bearing on this subject have appeared as follows: Bishop Tingle and Cram, *Am. Chem. J.*, **37**, 596 (1907); Bishop Tingle and Lovelace, *Ibid.*, **38**, 642 (1907); Bishop Tingle and Rolker, THIS JOURNAL, **30**, 1882 (1908); Bishop Tingle and Brenton, *Ibid.*, **31**, 1157 (1909); Bishop Tingle and Bates, *Ibid.*, **31**, 1233 (1909); Bishop Tingle and Brenton, *Ibid.*, **32**, 113 (1910).

the group R″ may replace R or R′ in the amidic acid, giving R″NHCOC₆
H₄CO₂H. This last acid may then eliminate water and form the imide
$C_6H_4 < {CO \atop CO} > NR''$. The amidic acids of the aliphatic series[1] do not ex-
hibit a similar series of reactions and consequently the formation of
substituted imides, under the influence of amines, could only be ascribed
to the influence of "the inherent nature of the benzene nucleus."

In the case of the phthalamidic acids the particular course which the
reaction takes, or the preponderating organic product, if more than one
is formed, is determined essentially by the nature of the groups R, R′, R″
which are linked to the nitrogen atoms of the amine or amidic group.

In the present paper we describe the results which we have obtained
in the course of an investigation of phthalamidic acids containing one
or more chlorine atoms or nitro groups in the benzene nucleus. In this
connection we have investigated a number of amidic acids derived from
3,6-dichloro-, etrachloro-, 3-nitro- and 4-nitrophthalic acids.

We have isolated *di-m-toluidine* and *di-p-chloroaniline 3,6-dichloro-
phthalates* and have materially improved Graebe's method for the prepara-
tion of 3,6-dichlorophthalophenylamidic acid, $C_6H_5NHCOC_6H_2Cl_2CO_2H$,
and of its anil. Our products appear to be superior in purity to those
described hitherto.

Unlike other members of this series, 3,6-dichlorophthalophenylamidic
acid does not appear to be dehydrated by the action of amines in solu-
tion, but it is very readily transformed into the anil $Cl_2C_6H_2 < {CO \atop CO} > NC_6H_5$,
by the action of 50 per cent. alcohol. It furnishes, therefore, another
example of the marked dehydrating power of even dilute alcohol. This
phenomenon was discussed in an earlier paper by Bishop Tingle and
Rolker.[2]

Entirely similar transformation results were observed with *tetrachloro-
phthalophenylamidic acid*, $C_6H_5NHCOC_6Cl_4CO_2H$. This acid is prepared
most conveniently from tetrachlorophthalic anhydride and aniline,
in benzene solution, but it may also be obtained by hydrolysis of the
phenylimide. Its *sodium* and *potassium salts* form colloidal solutions
in water; when these liquids are shaken, well-marked lathers are produced.

o-Toluidine and tetrachlorophthalic acid or its anhydride give what is,
apparently, *tetrachlorophthalo-o-tolylamidic acid*, $CH_3C_6H_4NHCOC_6Cl_4CO_2H$;
it is deposited in lustrous, white crystals, melting at 218–20°.

For comparison with the above phenylamidic acid we prepared *tetra-
chlorophthalo-β-naphthylamidic acid*, $C_{10}H_7NHCOC_6Cl_4CO_2H$, and the corre-
sponding *β-naphthylimide*, $C_6Cl_4 < {CO \atop CO} > NC_{10}H_7$. Both of these com-

[1] Bishop Tingle and Bates, *loc. cit.*

[2] THIS JOURNAL, **30**, 1884 (1908).

pounds are white, crystalline substances, melting at 287°, *i. e.*, the melting point of the imide. The β-naphthylamidic acid resembles the phenyl derivative in general properties, but it is somewhat less stable and is hydrolyzed by alkalies to its constituents with relative ease. Its transformation into the β-naphthylimide does not appear to be influenced by the presence of amines.

3-Nitrophthalophenylamidic acid, $C_6H_5NHCOC_6H_3(NO_2)CO_2H$, was prepared from the phenylimide.[1] When heated at about 100°, with alcohol (50%), it is changed slowly to a 3-nitrophthalodianilide, which is also formed, under similar conditions, in the presence of amines such as aniline, quinoline or *p*-toluidine. Our dianilide melted at 233–4° and is evidently isomeric with that of Chambers,[2] which melts at 211–2°. Chambers did not determine the structure of his compound, which was prepared from 3-nitrophthalyl chloride, but he pointed out that, according to theory, there should be three dianilides of 3-nitrophthalic acid, *viz.*
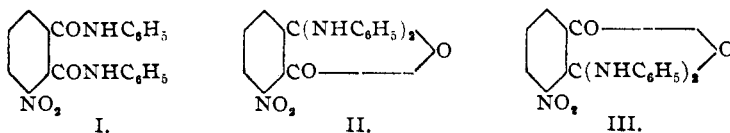
On account of its method of formation and of its higher melting point, our compound is probably the symmetrical derivative (I).

In this connection it is interesting to point out the effect of the nitro group in determining the production of the *dianilide* as the only product of the reaction. In the case of the compounds studied hitherto, the chief product has always been an imide, $C_6H_mX_n{<}^{CO}_{CO}{>}NR$ (X = H or Cl), a dianilide, if formed at all, being obtained only in very small quantity.

4-Nitrophthalophenylamidic acid, $C_6H_5NHCOC_6H_3(NO_2)CO_2H$, was prepared from the phenylimide obtained by Graebe and Buenzod,[3] or, more conveniently, by the action of aniline on 4-nitrophthalic anhydride. For the hydrolysis of the phenylimide Bogert[4] used baryta water; we find that an aqueous solution of potassium hydroxide is much more desirable. Our acid melted at 192°, not 181° as stated by Bogert, and, contrary to his experience, it dissolved without difficulty in a cold, aqueous solution of sodium carbonate. Our specimens of the phenylimide melted at 200–1°; Bogert[5] found 194°.

It is, perhaps, worth mentioning that the amidic acids, with which the senior author has worked during the past few years, frequently melt

[1] *Ber.*, **32**, 1992.
[2] THIS JOURNAL, **25**, 611.
[3] *Ber.*, **32**, 1993.
[4] THIS JOURNAL, **23**, 740.
[5] *Ibid.*, **23**, 757.

at temperatures about 15–20° lower than the melting points of the corresponding substituted imides, they then solidify and remelt at a higher temperature. It is found, however, that preparations which behave in this manner are almost always slightly impure. After further treatment they show the same melting point as the substituted imide and this temperature is always a degree or two higher than the second melting point mentioned above. It is, perhaps, hardly necessary to remark that, in every experiment which we have described, precautions have been taken in order to demonstrate that the final methods of purification which were adopted did not themselves convert the acids into their imides.

When heated on a boiling water bath, during 5 hours, with alcohol (50 per cent.), with and without the addition of quinoline, 4-nitrophthalophenylamidic acid is transformed, in part, into the phenylimide, the remaining acid being recovered unchanged. Under similar conditions, with alcohol (50 per cent.) and aniline, the same products are obtained, together with a small quantity of a *compound*, melting at 199–200°. In view of the results observed with the 3-nitro acid (see above) and from the fact that the new compound is not attacked by boiling with aqueous solutions of potassium hydroxide, or of hydrochloric acid, we conclude that the substance in question is probably *4-nitrophthalodianilide*, $O_2NC_6H_3(CONHC_6H_5)_2$.

A comparison of the results of the transformation experiments with 3-nitrophthalophenylamidic acid and those of the 4-nitro acid show that the approximation of negative groups $[CO_2H : CO_2H : NO_2 = 1 : 2 : 3]$ inhibits the formation of the phenylimide and greatly favors that of the dianilide. The opposite result is obtained when the nitro group is in the 4-position. It is, of course, easy to ascribe this inhibition of the imide formation to "steric hindrance," but we prefer to regard it as being due to a specific influence of the nitro group. The chief ground for this attitude is the fact that the 3,6-dichloro- and the tetrachlorophthalophenylamidic acids form phenylimides readily, although they show a specific insensibility to the transforming influence of amines.

4-Nitrophthalo-β-naphthylamidic acid, $C_{10}H_7NHCOC_6H_3(NO_2)CO_2H$, is prepared by mixing acetone or benzene solutions of β-naphthylamine and 4-nitrophthalic anhydride. After purification the acid is deposited in light yellow crystals, melting at 202–4°.

Camphorphenylamidic acid, $C_6H_5NHCOC_8H_{14}CO_2H$, was prepared by the method of Auwers and Schleicher,[1] from aniline and camphoric anhydride. *Camphor-β-naphthylamidic acid,* $C_{10}H_7NHCOC_8H_{14}CO_2H$, was obtained in a similar manner from β-naphthylamine. It is crystalline and melts at 220–1°. Neither of these acids was changed by prolonged

[1] *Ann.*, **309**, 341.

heating at the temperature of a boiling water bath, in presence of alcohol (50 per cent.), or of various amines.

In our earlier paper[1] we called attention to the readiness with which amidic acids of the phthalic series formed imides, $R<^{CO}_{CO}>NX$ (and other compounds), as compared with the stability in this respect of the analogous acids of the aliphatic series. Expressed in another way, the question is one of the relative stability of the substituted ammonium salts of the acids of the two series. After discussing the matter briefly, we reached the conclusion that the instability of the ammonium phthalamidates can be due only "to the inherent properties of the benzene nucleus," whatever this may mean.

Our object in preparing camphorphenyl- and β-naphthylamidic acids was to obtain further light on this point. They are the most readily available derivatives of the alicyclic series and, as stated above, their behavior is essentially similar to that of the corresponding aliphatic compounds. Consequently our previous conclusion, regarding the effect of the benzene nucleus, is still valid, but it may be supplemented by the statement that the accumulation and approximation of negative groups in the phthalic acid nucleus favors the formation of dianilides, $C_6XY(CONHC_6H_5)_2$, rather than that of imides, $C_6XY<^{CO}_{CO}>NR$.

Experimental.

1. DERIVATIVES OF 3,6-DICHLOROPHTHALIC ACID.—The following salts have been prepared: *Di-m-toluidine 3,6-dichlorophthalate*, $Cl_2C_6H_2(CO_2NH_3C_6H_4CH_3)_2$, is obtained as a light colored precipitate by mixing the acid and amine in concentrated, alcoholic solution. It is deposited, after recrystallization from water or alcohol, in light yellow crystals, melting at 176°. Found: N, 6.68; calculated, 6.28 per cent. *Di-p-chloroaniline 3,6-dichlorophthalate*, $Cl_2C_6H_2(CO_2NH_3C_6H_4Cl)_2$, is prepared in a similar manner from *p*-chloroaniline and 3,6-dichlorophthalic acid, in benzene solution. Light yellow crystals from water or alcohol, melting at 215°. Found: N, 5.90; calculated, 5.70 per cent.

Only tarry products were obtained by heating 3,6-dichlorophthalic acid with aniline or acetanilide, under various conditions of temperature, with and without solvents.

3,6-Dichlorophthalic anhydride was most easily prepared by heating the acid, at 40°, in a current of dry air, until water ceased to be evolved. The purification of the product is somewhat tedious. We found it best to dissolve the material in benzene and add a little gasoline. After a few hours a resinous deposit is formed on the sides of the container. The clear liquid is decanted and a little more gasoline added and the process

[1] THIS JOURNAL, 31, 1235.

repeated until no more resin is precipitated. To the clear liquid three or four volumes of gasoline are now added, whereupon the anhydride will be precipitated as a white powder. In order to purify it completely it may be necessary to dissolve it in a little benzene, at the ordinary temperature, and repeat the treatment with gasoline.

Preparation of 3,6-dichlorophthalanil and of 3,6-dichlorophthalophenyl-amidic acid.—We made numerous attempts to prepare these compounds by Graebe's method,[1] which consists in heating aniline 3,6-dichloro-phthalate. We varied the conditions rather widely, but at the best the yield of crude product was very poor and a great deal of it was lost because it was necessary to recrystallize it several times from acetic acid and to boil it with bone-black in order to obtain it in a condition of approximate purity. The small quantity of material which we obtained ultimately was hydrolyzed by means of an aqueous solution of potassium hydroxide. After acidification with hydrochloric acid a brownish precipitate was deposited; it was identified as 3,6-dichlorophthalophenyl-amidic acid by means of a mixed melting point.

Having found that Graebe's method was entirely unsuited for the preparation of the amidic acid, except in minute quantities, we devised the following process by which the acid may be obtained in a quantitative yield. Aniline (2 mols.) is added to 3,6-dichlorophthalic anhydride (1 mol.), dissolved in benzene. Water and potassium hydroxide (1 mol.) are then added and the mixture is boiled for some time and well stirred. After cooling, the benzene, which contains the excess of the aniline, is removed and the aqueous solution is acidified by means of hydrochloric acid. The resulting precipitate is light brown; this color appears to be due to the presence of a little impurity which is derived from the anhydride and which lowers the melting point of the amidic acid considerably. In order to remove this colored substance it was necessary to dissolve the crude acid in an aqueous solution of sodium hydrogen carbonate; this solution was boiled with bone-black, the acid reprecipitated and recrystallized twice from alcohol and twice from a mixture of benzene and gasoline. The 3,6-dichlorophthalophenylamidic acid, $C_6H_5NHCOC_6H_2Cl_2CO_2H$, which was ultimately obtained, was a light brown powder, melting at 165°. It dissolves readily in benzene, acetone, ether, alcohol, ethyl acetate and in a cold, aqueous solution of sodium carbonate. Found: Cl, 22.99; calculated, 22.90 per cent.

Transformations of 3,6-Dichlorophthalophenylamidic Acid.—The acid was not changed by dissolving it in benzene and heating the solution on a boiling water bath. The addition of aniline, quinoline, or β-naphthyl-amine produced no effect.

With 50 per cent. alcohol, instead of benzene, a part of the acid is trans-

[1] *Ber.*, **33**, 2019 (1900).

formed into the anil. The heating was continued during 35 minutes. The presence of aniline, quinoline, or β-naphthylamine does not appear to influence either the velocity or extent of this dehydration. These facts are discussed in the theoretical part of the present paper; they are of considerable interest in connection with the earlier work of Bishop Tingle and Rolker.[1]

We have found that 3,6-dichlorophthalanil, $Cl_2C_6H_2 < \overset{CO}{\underset{CO}{}} > NC_6H_5$, is most conveniently prepared, in the manner described above, by heating the amidic acid with alcohol. The product melts at 201°. Graebe's material, obtained by fusing the aniline salt, was evidently impure. It is stated to melt at 191°.

EXPERIMENTS WITH TETRACHLOROPHTHALIC ACID. *o-Toluidine and Tetrachlorophthalic Acid.*—*o*-Toluidine (2 mol.) and the acid or anhydride were mixed in acetone solution. The precipitate which forms immediately was purified by solution in water or ethyl acetate, from either of which it is deposited in lustrous white crystals. It melts at 218-20° and is probably tetrachlorophthalo-*o*-tolylamidic acid, $CH_3C_6H_4NHCOC_6Cl_4CO_2H$. Found: N, 3.95; calculated, 3.56 per cent.

Preparation of Tetrachlorophthalophenylimide and of Tetrachlorophthalophenylamidic Acid.—The phenylimide was prepared by Graebe and Buenzod's method, which consists in the fusion of aniline tetrachlorophthalate.[2] The yield is quite poor and it is difficult to purify the product.

Tetrachlorophthalophenylamidic acid, $C_6H_5NHCOC_6Cl_4CO_2H$, may be obtained by boiling the anil, during 2-3 hours, with a rather concentrated aqueous solution of potassium hydroxide, but it is prepared much more easily by adding aniline to tetrachlorophthalic anhydride, both in benzene solution. The precipitate which forms immediately is collected and is purified by dissolving it in a warm, aqueous solution of sodium carbonate and subsequently adding hydrochloric acid. It is readily soluble in acetone, ether, or ethyl acetate and is deposited from alcohol in white crystals, melting at 266°, *i. e.*, at the same temperature as the anil. Specimens which have been insufficiently purified melt about 230°, then become solid and finally remelt a little below 266°. Found: N, 3.76; calculated, 3.69 per cent.

In aqueous solution the acid reddens litmus paper immediately and it dissolves without difficulty in warm, aqueous solutions of alkali hydroxides, but cold solutions attack it only slowly because its *sodium* and *potassium salts* are colloidal and soapy and readily form lathers. · When a warm aqueous solution of either of these salts is cooled it becomes turbid, then jelly-like and finally, if the liquid is sufficiently concentrated, a tarry or resinous precipitate is formed.

[1] *Loc. cit.*
[2] *Ber.*, **32,** 1994.

Transformations of Tetrachlorophthalophenylamidic Acid.—The acid was recovered unchanged after boiling during 35 minutes in benzene solution. The addition of aniline was without effect. In 50 per cent. alcohol, on a boiling water bath, a part of the acid is transformed into the anil. The reaction does not appear to be influenced by the presence of aniline, or of β-naphthylamine.

On account of their identical melting points, as mentioned above, some trouble was at first encountered in distinguishing between tetra-chlorophthalophenylamidic acid and the phenylimide; this difficulty is increased by the fact that the acid does not dissolve easily in a cold, aqueous solution of potassium hydroxide. The most ready methods of identification were the solubility of the acid in a boiling, aqueous solution of sodium carbonate and the fact that the aqueous solution of the acid reddens litmus paper. Tetrachlorophthalophenylamidic acid changes slowly to the phenylimide at the ordinary temperature, consequently the material employed for the transformation experiments described above was carefully purified by means of sodium carbonate solution immediately before use.

Tetrachlorophthalo-β-naphthylamidic Acid.—This acid, $C_{10}H_7NHCOC_6$ Cl_4CO_2H, is prepared from β-naphthylamine and tetrachlorophthalic anhydride, in a simliar manner to the phenyl derivative. The *sodium* and *potassium salts* dissolve with difficulty in water, at the ordinary temperature and the resulting solutions are colloidal, consequently it is somewhat troublesome to separate the amidic acid from unchanged β-naphthylamine. The best plan we found was to add dilute hydrochloric acid to a boiling aqueous solution of the sodium salt, collect the precipitated acid and boil it with a large quantity of water; after drying it is treated with a mixture of toluene and glacial acetic acid; from this it deposits in white crystals, melting at 287°, which is the m. p. of the β-naphthylimide. It dissolves readily in ethyl acetate, acetone and in 95 per cent. alcohol, is less soluble in ether, chloroform and in 50 per cent. alcohol and is practically insoluble in benzene. Found: N, 3.23; calculated, 3.26 per cent.

The acid changes slowly, at the ordinary temperature, to the β-naphthyl-imide. Concentrated, aqueous potassium hydroxide solution hydro-lyzes it slowly to β-naphthylamine and tetrachlorophthalic acid, both of which were fully identified.
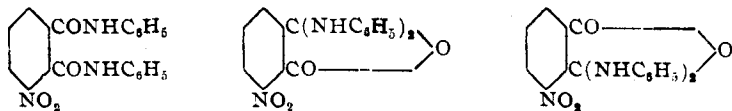
Highly purified tetrachlorophthalo-β-naphthylamidic acid is trans-formed into the β-naphthylimide when heated with alcohol of 95 or 50 per cent. The change was not complete during the time of our experi-ments, about 35 minutes, and the reaction does not appear to be in-fluenced by the addition of aniline or β-naphthylamine to the alcoholic solution.

Tetrachlorophthalo-β-naphthalo-β-naphthylimide, $C_6Cl_4 < {CO \atop CO} > NC_{10}H_7$, is prepared by heating the acid at 260–70°, during 10 minutes. It is soluble in acetone, ethyl acetate, or alcohol and is deposited in white crystals, melting at 287°. The compound does not dissolve in an aqueous solution of sodium carbonate, but by the action of a warm, aqueous solution of potassium hydroxide it is hydrolyzed slowly to potassium tetrachlorophthalo-β-naphthylamidate, which, of course, goes into solution.

DERIVATIVES OF 3-NITROPHTHALIC ACID.—3-Nitrophthalophenylamidic acid, $C_6H_5NHCOC_6H_3(NO_2)CO_2H$, was prepared by the hydrolysis of the phenylimide. We found that this was readily accomplished by warming with an aqueous solution of potassium hydroxide, in place of the barium hydroxide employed by Bogert.[1] After several recrystallizations from ethyl acetate our material melted at 181° and, contrary to the statement of Bogert,[2] dissolved readily in an aqueous solution of sodium carbonate, at the ordinary temperature.

Transformation of 3-Nitrophthalophenylamidic Acid.—At the temperature of a boiling water bath, during 35 minutes, the acid is not changed in presence of alcohol (50 per cent.), or of quinoline, but on adding aniline to the alcohol a little 3-nitrophthalodianilide is produced and the yield of this compound is quantitative if the heating is prolonged during 5 hours. With *p*-toluidine or alcohol (50 per cent.), during 5 hours' heating, the acid also gives a small quantity of the same dianilide. This *dianilide* was obtained in crystals, melting at 233–4°. It is readily soluble in alcohol, chloroform, ether, acetone, or ethyl acetate, but dissolves with difficulty in benzene, or toluene. The compound is not attacked by a boiling, aqueous solution of potassium hydroxide, nor by hydrochloric acid. Found: C, 66.76; H, 4.66. Calculated: C, 66.48; H, 4.15 per cent.

Our 3-nitrophthalodianilide appears to be isomeric with one prepared by Chambers[3] from 3-nitrophthalyl chloride. It is uncertain which of the three possible structures

$$\begin{array}{l} \text{CONHC}_6\text{H}_5 \\ \text{CONHC}_6\text{H}_5 \\ \text{NO}_2 \end{array} \qquad \begin{array}{l} \text{C(NHC}_6\text{H}_5)_2 \\ \text{CO} \end{array}\!\!\!> O \qquad \begin{array}{l} \text{CO} \\ \text{C(NHC}_6\text{H}_5)_2 \end{array}\!\!\!> O$$

are to be assigned to the two compounds in question, but we think that ours is probably the symmetrical derivative.

3-Nitrophthalic Anhydride and β-Naphthylamine.—When these substances are mixed in an organic solvent, a compound is precipitated

[1] THIS JOURNAL, **23**, 740.

[2] *Loc. cit.*

[3] THIS JOURNAL, **25**, 611.

which appears to be *3-nitrophthalo-β-naphthylamidic acid*, $C_{10}H_7NHCOC_6$ $H_3(NO_2)CO_2H$. Its purification is attended with considerable difficulty on account of the progressive formation of an oily material. We obtained light yellow crystals from a mixture of acetone, benzene and chloroform; they melted at 201–2° and dissolved easily in alcohol, ethyl acetate, acetone, or ether, less readily in chloroform. That the compound is an acid is shown by the fact that it is soluble in an aqueous solution of sodium carbonate and is reprecipitated on acidification with hydrochloric acid. The quantity of purified material ultimately available was too small to permit of analysis.

DERIVATIVES OF 4-NITROPHTHALIC ACID.—4-Nitrophthalophenylamidic acid, $C_6H_5NHCOC_6H_3(NO_2)CO_2H$, was obtained from the phenylimide, which was prepared by Graebe and Buenzod's method.[1] This consists in heating aniline 4-nitrophthalate. The resulting anil, after purification, was dissolved in a warm, aqueous solution of potassium hydroxide, the heating continued during about 5 minutes and the amidic acid precipitated by means of dilute hydrochloric acid. The acid was then crystallized several times from ethyl acetate, in order to separate it from tarry matter which is always produced during the fusion of the aniline 4-nitrophthalate.

The phenylamidic acid may also be obtained by mixing benzene solutions of aniline and 4-nitrophthalic anhydride. The product obtained in this manner is less difficult to purify than that prepared from the anil. The acid was dissolved in a cold, aqueous solution of sodium carbonate, reprecipitated by means of dilute hydrochloric acid and recrystallized several times from ethyl acetate. Our acid melted at 192°. The method of preparation given above is much more convenient than that described by Bogert.[1] He hydrolyzed the anil by the use of barium hydroxide, added sulphuric acid and extracted the amidic acid by means of alcohol. His product melted at 181°, and did "not appear to decompose carbonates." Our material dissolved in a cold, aqueous solution of sodium carbonate after 10–15 minutes. Bogert gives 194° as the m. p. of 4-nitrophthalophenylimide.[2] Our preparation melted at 200–1°.

We refer, in the first part of this paper, to a peculiarity shown by the acids of this series in regard to their melting points.

Transformation of 4-Nitrophthalophenylamidic Acid.—At the temperature of a boiling water bath, after 5 hours, in presence of alcohol (50 per cent.), a part of the acid was recovered unchanged, the remainder being converted into the phenylimide. A similar result was obtained by adding quinoline to the solution. After 6 hours' heating, under similar conditions, with a mixture of alcohol (50 per cent.) and aniline,

[1] *Loc. cit.*
[2] *Ibid.*, p. 757.

the products consisted of unchanged acid, phenylimide and a *compound*, melting at 199–200°. It was not attacked by boiling with aqueous solutions of potassium hydroxide, or hydrochloric acid; boiling with alcoholic solutions of the same reagents produced only a slight effect. These results lead to the conclusion that the substance is probably *4-nitro-phthalodianilide*, $O_2NC_6H_3(CONHC_6H_5)_2$, which does not appear to have been described hitherto. The material available was insufficient for an analysis.

Preparation of 4-Nitrophthalo-β-naphthylamidic Acid.—This acid, $C_{10}H_7NHCOC_6H_3(NO_2)CO_2H$, was prepared by adding β-naphthylamine to 4-nitrophthalic anhydride, both substances being dissolved in acetone, or benzene. The precipitate which is formed is collected, dried, dissolved in an aqueous solution of potassium hydroxide, the liquid acidified with hydrochloric acid and the precipitated solid recrystallized several times from a mixture of acetone and benzene. In this manner we obtained the acid in light yellow crystals, melting at 202–4°. It dissolves in a cold, aqueous solution of sodium carbonate and is reprecipitated by hydrochloric acid. The acid is readily soluble in acetone, ethyl acetate, alcohol, or ether, less readily in chloroform and practically insoluble in benzene. Found: N, 8.21; calculated, 8.33 per cent.

DERIVATIVES OF CAMPHORIC ACID.—Camphorphenylamidic acid, $C_6H_5NHCOC_8H_{14}CO_2H$, was prepared without difficulty by the method of Auwers and Schleicher;[1] it consists in boiling camphoric anhydride, aniline and chloroform during 3 hours. The product was recrystallized from alcohol.

Camphor-β-naphthylamidic acid, $C_{10}H_7NHCOC_8H_{14}CO_2H$, was prepared in a similar manner to the phenyl derivative, except that the heating was continued during 5 hours. The chloroform was then evaporated, the residue dissolved in a warm, aqueous solution of sodium bicarbonate and the amidic acid precipitated from the clear solution by means of hydrochloric acid. After solution in alcohol the compound was obtained in white crystals, melting at 220–1°. Found: N, 4.39; calculated, 4.30 per cent.

The acid dissolves readily in acetone, alcohol, ethyl acetate, chloroform, or ether; it is slightly soluble in benzene and in hot water. In solution the acid reddens blue litmus paper and it dissolves in a warm, aqueous solution of sodium carbonate. The *sodium* and *potassium salts* are somewhat colloidal and soapy.

Neither camphorphenyl- nor β-naphthylamidic acids could be transformed into the imides at the temperature of a boiling water bath. The experiments were made in alcoholic solution (50 per cent.), the heating continuing during 35 minutes in the case of the phenyl compound and

[1] *Ann.*, **309**, 341.

6 hours in that of the β-naphthyl derivative. The addition of aniline or quinoline to the alcoholic solution of the phenylamidic acid and of β-naphthylamine to that of the β-naphthylamidic acid produced no effect. It is clear, therefore, that these two acids resemble the aliphatic amidic acids and differ from those of the aromatic series.

Summary.

1. We have prepared a number of phthalamidic acids of the type $RNHCOC_6XCO_2H$, where R = phenyl or β-naphthyl and X represents H_2Cl_2, Cl_4 or H_3NO_2.

2. The behavior of these acids when heated with alcohol alone and also with alcohol and amines has been studied.

3. The accumulation and approximation of negative groups in the phthalic acid nucleus favors the formation of diamides, $C_6X(CONHR)_2$, rather than that of imides, $C_6X <{CO \atop CO}> NR$.

4. Camphoramidic acids, $RNHCOC_8H_{14}CO_2H$, $(R = C_6H_5$ or β-naphthyl) resemble the corresponding aliphatic acids and not those of the aromatic series. They are stable under the conditions employed.

5. A number of new compounds are described, and improved methods have been worked out for the preparation and purification of certain substances which had been obtained previously by other chemists.

The investigation is being continued in various directions.

McMASTER UNIVERSITY.
TORONTO, CANADA.

THE BASIC PROPERTIES OF OXYGEN: COMPOUNDS WITH BRO-MINE AND IODINE.

BY D. McINTOSH.

Two addition compounds of ether and bromine are known. One, which we may call the tribromide (m. p. 22°)[1] consists of three, and the other, the dibromide (m. p. —40°)[2], of two atoms of bromine to a molecule of ether.

The constitution of the dibromide may be explained in several ways, assuming the oxygen to be quadrivalent and the bromine uni- or tri-valent. The tribromide, however, can be conveniently expressed only by doubling the formula and writing it $C_4H_{10}O = Br — Br = Br —$ $Br = Br — Br = OH_{10}C_4$; and as nothing is known against this mode of representing the dibromide, either in regard to its molecular weight or its reactions, its formula, too, may be doubled, $(C_4H_{10}O = Br —$ $Br = Br — Br = OH_{10}C_4)$.

[1] Schützenberger, *Ann.*, **167**, 86 (1873).
[2] *Trans. Chem. Soc.* (London) **87**. 784 (1905).