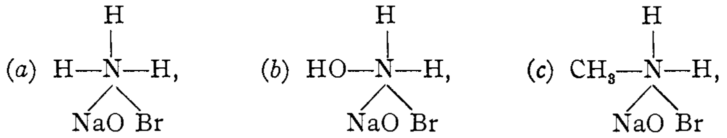
0.0115 gram—or 55 per cent.[1] of the nitrogen was evolved. Nitric acid[2] was found in the solution.

Ammonia.—When 1 cc. of ammonium chloride solution, standardized by 0.1 *N* silver nitrate and containing 0.00613 gram ammonia, was treated in a nitrometer with sodium hypobromite at 742 mm. and 21.5°, (*a*) 4.66 cc. N_2 and (*b*) 4.64 cc. N_2 were obtained—calculated volume was 4.65 cc. N_2.

Now since urea and ammonia quantitatively evolve nitrogen, since guanidine and semicarbazide evolve two-thirds of their nitrogen, since hydroxylamine evolves about one-half of its nitrogen, since methylamine slowly evolves its nitrogen, and since urethane almost fails to evolve nitrogen, it is concluded that, when treated with sodium hypobromite, the mere presence in a compound of the *amino group* is not a criterion of evolution of nitrogen. *The influence of other groups* in the compound mentioned is a greater factor. If the reaction of sodium hypobromite with these compounds were purely *ionic*, certainly greater similarity of reaction is expected. However, if there are formed different aggregates as

(X)



$$(a)\ H-\overset{H}{\underset{NaO\quad Br}{N}}-H, \qquad (b)\ HO-\overset{H}{\underset{NaO\quad Br}{N}}-H, \qquad (c)\ CH_3-\overset{H}{\underset{NaO\quad Br}{N}}-H,$$

either representing respectively different stabilities, or ease of dissociation, or representing in the same aggregate tendencies to dissociate in more than one direction, a more rational basis of interpretation of these organic reactions is revealed. Studies will be continued along these lines with compounds containing two atoms of carbon.

SEATTLE, WASH., June 24, 1909.

ACTION OF AMINES ON DIBASIC ALIPHATIC ACIDS. FIFTH COMMUNICATION ON AMIDIC ACIDS.[3]

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

Received September 4, 1909.

With the exception of the work on succinic acid, described in the first paper of this series, attention has, hitherto, been directed exclusively to the interaction of amines with phthalic acid and its substitution products. In the present communication we describe the results which we

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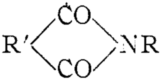
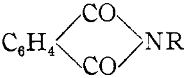
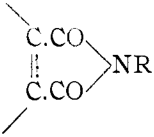
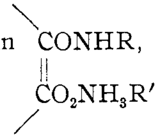
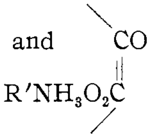
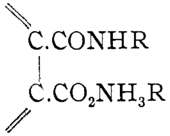
[1] Cf. with NaOCl, *Ber.*, 20, 1504.

[2] All of the other nitrogen-containing compounds failed to give solutions containing nitric acid.

[3] 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).

have obtained by extending the investigations of Bishop Tingle and Cram to other aliphatic dibasic acids. We have examined the behavior of certain amines, usually aniline and β-naphthylamine, with oxalic, succinic, fumaric, maleic, malic, citraconic and tartaric acids. The amidic acids, RNHCO * * * CO_2H, of this series which we have prepared, have been investigated with regard to their ability to transform into imides,  $R'\langle{}^{CO}_{CO}\rangle NR$, or into amides, RNHCO * * * CONHR, by the action of amines of various types. Under conditions in which phthalamidic acids, $RNHCOC_6H_4CO_2H$, are converted very readily into imides,  $C_6H_4\langle{}^{CO}_{CO}\rangle NR$, the aliphatic amidic acids are quite stable and even much more prolonged heating, at higher temperatures than were used with the phthalamidic acids, failed to effect their transformation.

It has been shown by Bishop Tingle and Rolker[1] that this condensation to the imide is preceded by the formation of a substituted ammonium phthalamidate, $RNHCOC_6H_4CO_2NH_3R'$, which, under the experimental conditions employed, is generally highly unstable. The question at once arises as to why these salts should be so markedly different in this respect from the ammonium aliphatic amidates, RNHCO * * * CO_2NH_3R. Our work has shown that their instability is not due to the nature of the groups R and R′ in the amine residues, nor is it caused by the tendency to form a five-membered ring, because such a cycloid exists both in the phthal- and succinimides. The stability of the fumar- and maleanilic acids proves that the transformation of the phthalic derivatives is not produced by the presence of the double linkage in the complex,  $\begin{matrix} \diagdown \\ C.CO \\ \| \\ C.CO \\ \diagup \end{matrix}\rangle NR$, nor can it be due to any specially favorable stereometric arrangement of the amidic and carboxylic radicles as in  $\begin{matrix} \diagdown CONHR \\ \| \\ CO_2NH_3R' \\ \diagup \end{matrix}$, and  $\begin{matrix} \diagdown CONHR \\ \| \\ R'NH_3O_2C \\ \diagup \end{matrix}$, for example.

We may regard the phthalamidic acids, or their ammonium salts, as existing in the primary phase of the Kekulé formula,  $\begin{matrix} \diagdown\!\!\diagdown C.CONHR \\ | \\ C.CO_2NH_3R \\ \diagup\!\!\diagup \end{matrix}$,

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[1] *Loc. cit.*

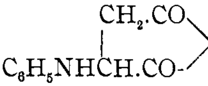
i. e., with a single linkage between the tertiary carbon atoms instead of the double one shown in the imide formula given above. This linkage would correspond with that of the succinamidic acids, $RNHCOCH_2.CH_2CO_2H$, which, as previously mentioned, we have found to possess a relatively high degree of stability.

Assuming the validity of these considerations, we are driven to regard the lack of stability of the ammonium phthalamidates as being due to the inherent properties of the benzene nucleus. We hope to test the question still further by extending the investigation to the di-, tetra- and hexahydrophthalamidic acids.

Oxanilic acid is not changed by heating with ethyl or methyl alcohols, or with toluene, at 100°, during 35 minutes. Under similar conditions, in presence of aniline, quinoline, pyridine or β-naphthylamine it forms with each base an *ammonium salt.* All of these crystallize readily and are quickly resolved into the parent acid and base by the action of either potassium hydroxide or hydrochloric acid. The addition of dilute hydrochloric acid to potassium oxanilate produces a crystalline *acid salt*, $C_6H_5NHCOCO_2K.C_6H_5NHCOCO_2H$.

We were unable to prepare oxal-β-naphthylamidic acid by the method described in the literature.[1]

Succin-β-naphthylamidic acid melts at 184–185°, not 190–192°. It is not changed when heated at 100°, during 35 minutes, with alcohol or toluene, either alone or when mixed with aniline, quinoline, or β-naphthylamine, respectively.

In alcoholic or ethereal solution, at the ordinary temperature, fumaric acid and aniline form the *aniline hydrogen salt*, $C_6H_5NH_3O_2CCH : CHCO_2H$, melting at 185°. No dianiline salt could be obtained. At 160–170°, aniline and fumaric acid yield only phenylaminosuccinphenylimide (phenylasparaginanil),  $\left.\begin{array}{l} CH_2.CO \\ \quad | \\ C_6H_5NHCH.CO \end{array}\right\rangle NC_6H_5$, which, hitherto, does not appear to have been obtained from fumaric acid.

We were unable to prepare fumaranilic acid by Bischoff's method,[2] but we obtained it, without difficulty, from fumaryl chloride and aniline, in ethereal solution. When heated at 100°, with aniline alone, the anilic acid forms phenylasparaginanil, but at 65°, in alcoholic solution, aniline does not attack the acid.

Maleanilic acid was obtained without difficulty from maleic anhydride

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[1] *Mitt. Technol. Gewerb. Mus. Vienna* [ii], **8,** 316 (1899). I wrote to Professor Friedländer on Aug. 1st, telling him of this result and asking him if he could supply any details regarding the preparation of the compound, or if he would send a copy of his original paper, which is inaccessible to me. Up to the present (Oct. 11) no reply has been received.—J. B. T.

[2] *Ber.*, **24,** 2003.

and aniline, by Anschütz's method.[1] When heated during 35 minutes, at 100°, the anilic acid is not attacked by quinoline alone, or in presence of a solvent, the same is true of aniline, at 65°, but at 100°, without a solvent, aniline converts the acid into phenylasparaginanil.

Malic acid and aniline, when mixed and distilled under reduced pressure, form maleanilic acid and phenylasparaginanil; the production of this latter substance, in the manner described, appears to be new.

We encountered great difficulties in the preparation of malanilic acid, the method described by Arppe[2] proving to be entirely unworkable in our hands. We finally obtained, by a different method, a substance which we think is the anilic acid. It melts at 155° and when heated with aniline, at 100°, forms what is probably a *salt*. This melts at 110°. Arppe's anilic acid is stated to melt at 145°. The quantity of substance at our disposal was too small to admit of analysis. Some of the difficulties inherent in the preparation of malanilic acid are pointed out in the experimental portion of this paper.

Pseudoitaconanilic acid was prepared from itaconic acid by a slight modification of Gottlieb's method.[3] It was not changed at 100° by aniline alone, or in presence of the various solvents which were employed.

At the ordinary temperature, in well-dried ethereal solution, and also at about 100° without any solvent, citraconic acid and aniline form what is probably anilinopyrotartaric acid, $CH_3C(NHC_6H_5)(CO_2H)CH_2CO_2H$, melting at 170–171°.[4] Gottlieb states[5] that aniline and citraconic acid, at 100°, form the anilic acid, but we were unable to detect the presence of any of this substance in the products of our experiments.

Tartranilic acid was prepared by a modification of Arppe's method,[6] which consisted in hydrolyzing the tartranil with an aqueous solution of potassium hydroxide instead of employing aqueous ammonia. Tartranilic acid forms *salts* with all the amines which we investigated. In no case was there the slightest indication of the production of any *N*-substituted imide. The *aniline* and *quinoline salts*, melting at 149–150° and 129–130°, respectively, were obtained at 100°, although it is practically certain that, like the *β-naphthylamine salt*, they could be prepared at the ordinary temperature. This last salt melts at 176–177° and is formed in alcoholic solution. When heated at 180°, it is converted into what is probably *tartarphenyl-β-naphthyldiamide*, $C_6H_5NHCOCH(OH)CH(OH)CONHC_{10}H_7$, which melts at 240–242° and is also produced by heating *aniline tartar-β-naphthylamidate*, see below.

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[1] *Ber.*, **20**, 3215.

[2] *Ann.*, **96**, 111.

[3] *Ibid.*, **77**, 284.

[4] Schiller, *Ber.*, **18**, 1046. Reissert, *Ibid.*, **21**, 1362.

[5] *Loc. cit.*, p. 277.

[6] *Ann.*, **93**, 355.

Tartaric acid and β-naphthylamine give a small yield of *tartar-β-naphthylamidic acid*, $C_{10}H_7NHCOCH(OH)CH(OH)CO_2H$, the purification of which was attended with a considerable loss of material. It melts at about 180° when heated very quickly, evolves water, becomes solid and then remelts at 220°, doubtless forming an *imide*. With aniline the amidic acid yields a *salt*, melting at 172–174°. The salt, when melted, evolves water and gives tartarphenyl-β-naphthyldiamide (m. p. 240–242°), as mentioned above. This behavior is interesting because it is the first example with which we are acquainted, of the formation of any unsymmetrical *N*-substituted diamide in the aliphatic series. Similar compounds, derived from phthalamidic acids, have been described recently by Bishop Tingle and Rolker[1] and Bishop Tingle and Brenton.[2]

Experimental.

Oxanilic Acid.—It was found to be desirable to modify in some details the method given by Aschan[3] for the preparation of this compound. After heating oxalic acid (1 mol.) with aniline (2 mols.), the resulting aniline oxanilate is dissolved in the smallest requisite quantity of boiling water, acidified with a little less sulphuric acid than Aschan specifies, and the liquid allowed to cool. The mixed precipitate of aniline oxanilate and oxanilic acid was removed, washed with cold water, dried in air and the anilic acid extracted by means of hot toluene. Aniline oxanilate melts indefinitely between 140–160° according to the rapidity of heating. On account of this fluctuating melting point and because its appearance is similar to that of oxanilic acid, there is some difficulty in distinguishing between the two substances, the mixed melting point test being, of course, indecisive. We found that, on the whole, the most convenient method was to fuse the material, either directly over a flame or in an oil bath. The acid is not chemically changed by this treatment and, after fusion, it dissolves readily in warm water. The aniline salt, on the other hand, forms oxanilide when melted and this dissolves with difficulty in hot water.

Oxanilic acid is not affected by heating during 35 minutes, at 100°, with ethyl or methyl alcohol, or toluene. Under similar conditions, *aniline* transforms it completely into aniline oxanilate.

With quinoline the acid forms the *quinolinium salt*; colorless crystals melting at 122–3°. It is readily soluble in hot water and in alcohol, more sparingly in chloroform, ether, or cold water. From any of these solvents the salt may be deposited as a yellow oil, which after a time changes to the white crystals. The salt is most conveniently purified by allowing its alcoholic solution to evaporate spontaneously. With an aqueous solution of potassium hydroxide the salt liberates quinoline whereas hydrochloric acid precipitates oxanilic acid from it.

Pyridinium oxanilate is prepared in a similar manner to the quinolinium compound. It is deposited in colorless crystals, melting at 132–133°. It dissolves readily in hot alcohol or water, more sparingly in benzene, and is insoluble in ether. Hydrochloric acid precipitates oxanilic acid from it and an aqueous solution of potassium hydroxide liberates pyridine.

β-Naphthylammonium oxanilate, obtained in a similar manner, forms pink crystals, melting at 151°. It dissolves in alcohol or water, but is less soluble in toluene

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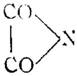
[1] THIS JOURNAL, **30**, 1882 (1908).

[2] *Ibid.*, **31**, 1157 (1909).

[3] *Ber.*, **23**, 1820 (1890).

and insoluble in ether. A mixture of it with an equal quantity of oxanilic acid melts at 135–140°. With hydrochloric acid and potassium hydroxide, respectively, it behaves like the other salts.

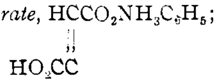
Potassium hydrogen oxanilate, $C_6H_5NHCOCO_2K.C_6H_5NHCOCO_2H$, was prepared by adding dilute hydrochloric acid slowly to a saturated aqueous solution of potassium oxanilate, until no further precipitate is formed. The salt was then dried and extracted with ether to remove any traces of oxanilic acid. It dissolves readily in alcohol or water and its solutions are acid to litmus. With hydrochloric acid in excess it forms oxanilic acid. Analysis showed that it had the composition given above.

The ammonium salts described above were the only substances which we could isolate from the products of the interaction of the amines and oxanilic acid; no trace of any imide,  $\begin{matrix}CO\\|\\CO\end{matrix}\!\!>NR$, could be discovered.

Oxalic Acid and β-Naphthylamine.—A considerable number of experiments were made, under varying conditions, in order to prepare oxal-β-naphthylamidic acid, $C_{10}H_7NHCOCO_2H$, but without success. The compound has been described by P. Friedländer, Heilpern and Spielfogel[1] as being produced at 140–150°, from crystallized oxalic acid and β-naphthylamine. Unfortunately their original paper is not accessible to us.

Succinic Acid and β-Naphthylamine.—A good yield of succin-β-naphthylamidic acid was obtained by Pellizzari and Matteucci's method,[2] which consists in heating the mixture of acid and base at 200°, hydrolyzing the resulting imide with potassium hydroxide and acidifying the solution. Our preparation of the acid melted at 184–185°, thus confirming the observation of Auwers,[3] whereas the Italian chemists give the melting point as being 190–192°.[4]

The acid is not changed by heating, at 100°, with aniline, quinoline, or β-naphthylamine, in presence of alcohol, or toluene, during 35 minutes.

Fumaric Acid and Aniline—These substances combine in alcoholic or ethereal solution, at the ordinary temperature, giving *aniline hydrogen fumarate*,  $\begin{matrix}HCCO_2NH_3C_6H_5\\ \|\\ HO_2CC\end{matrix}$; colorless crystals, melting at 185°. It dissolves readily in warm water or in alcohol, is less soluble in benzene and only slightly so in ether. N: found, 7.13; calculated, 6.7 per cent.

When added to an aqueous solution of potassium hydroxide or of sodium carbonate, aniline is liberated from the salt and fumaric acid is produced by the action on it of hydrochloric acid at the ordinary temperature.

By treating fumaric acid with two molecular proportions of aniline, under the conditions described above, half the aniline remained uncombined and the remainder formed the monoaniline salt.

When heated during 30 minutes, at 160–170°, fumaric acid and aniline (1 or 2 molecules) form only phenylasparaginanil, which does not appear to have been prepared previously from fumaric acid.

According to Bischoff,[5] fumaranilic acid is produced by hydrolyzing fumaranilide, $C_6H_5NHCOCH : CHCONHC_6H_5$, with alkali. We employed both aqueous and alco-

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[1] *Mitt. Technol. Gewerb. Mus. Vienna* [ii], **8**, 316 (1899).

[2] *Ann.*, **248**, 159.

[3] *Ibid.*, **292**, 190.

[4] *Loc. cit.*

[5] *Ber.*, **24**, 2003.

holic solutions of potassium hydroxide, under varied conditions of concentration and temperature, but failed entirely to obtain any of the desired acid.

The following method, however, gave the acid in fairly good yield. Aniline is dissolved in ether and the solution added gradually to fumaryl chloride, in the same solvent. After removal of the ether, fumaranilic acid is extracted from the residue by means of warm water.

When heated at 65°, during 35 minutes, with alcohol or with an alcoholic solution of aniline, fumaranilic acid is not changed, but with aniline alone, at 100°, phenylasparaginanil is produced.

Maleic Acid and Aniline.—Maleanilic acid, $C_6H_5NHCOCH : CHCO_2H$, was prepared, without difficulty, by Anschütz's method,[1] from aniline and maleic anhydride, in ethereal solution. It is not necessary to use absolute ether, as Anschütz states, although the ether should be of good quality.

When heated at 100°, during 35 minutes, the anilic acid is not changed in presence of alcohol (98 per cent.), benzene, or toluene, nor in that of quinoline alone, or mixed with one of these solvents. At 65°, during the same interval of time, aniline alone, or in solution, is also without action on the acid, but at 100°, during 35 minutes, without any solvent, aniline and the acid form phenylasparaginanil.

Malic Acid and Aniline.—When these substances were mixed and distilled under reduced pressure, we obtained, in addition to maleanilic acid, phenylasparaginanil, the formation of which, in this manner, has not hitherto been recorded.

Malanilic acid has been described by Arppe,[2] who prepared it by hydrolysis of the anil with aqueous ammonia. In spite of numerous efforts, under varied experimental conditions, we were entirely unsuccessful in obtaining any of the acid by this method. No better results were produced by the use of barium hydroxide as the hydrolyzing agent, but by warming the anil with a concentrated aqueous solution of potassium hydroxide, then cooling thoroughly and adding the calculated quantity of hydrochloric acid, a small portion of what is probably malanilic acid is deposited. It is necessary to use rather highly concentrated solutions and to evaporate the liquid somewhat, after acidification.

The difficulties attendant on the preparation of malanilic acid are very considerable; they arise partly from the fact that aniline and malic acid, or the anhydride, may react in several different ways which, in some cases, may give rise to stereoisomeric derivatives, so that in any event the yield of a single homogeneous product would be relatively small. Difficulties of another order are due, as Arppe points out, to the ready solubility of the anilic acid in water and to the fact that it is hydrolyzed by dilute mineral acids both at the ordinary temperature and when warmed.

Our product was obtained in such small quantity that we do not consider it necessary to give our method of preparation in greater detail because we do not regard it as being satisfactory. The substance melted at 155°, not 145° as Arppe states, but we failed to obtain enough for analysis.

At 100°, with aniline alone, it forms what may be an *aniline salt*, which melts at 110°.

Itaconic Acid and Aniline. Preparation of Pseudoitaconanilic Acid.—Pseudoitaconanilic acid was prepared essentially by Gottlieb's method.[3] Itaconic acid was heated with aniline (1 mol.), at 100–150°, during 20 minutes. The product was powdered, washed with ether and then boiled with water to remove any traces of citraconic and itaconic acids. The yield was good.

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[1] *Ber.*, **20**, 3215.

[2] *Ann.*, **96**, 111.

[3] *Ibid.*, **77**, 284.

When heated at 100°, during 35 minutes, with aniline alone, or in solution of nitrobenzene, toluene, or alcohol (50 per cent.), pseudoitaconanilic acid undergoes no change.

Citraconic Acid and Aniline.—When well-dried ethereal solutions containing equimolecular proportions of citraconic anhydride and aniline are mixed, a substance is deposited which, after purification, melts at 170–171°. It is soluble in an aqueous solution of sodium carbonate, is reprecipitated by acids and dissolves without difficulty in alcohol or in warm chloroform. The compound reduces silver nitrate. It is also prepared by heating aniline and citraconic acid at a little above 100°. The resulting product is warmed with an aqueous solution of potassium hydroxide and the clear liquid acidified with hydrochloric acid. According to Gottlieb[1] this procedure should give citraconanilic acid, but we were unable to detect the presence of any of that substance in the products of the reaction. Our compound (m. p. 170–171°) is probably anilinopyrotartaric acid, $CH_3C(NHC_6H_5)(CO_2H)CH_2CO_2H$. We were successful in preparing some citraconanil by Gottlieb's method.[1]

Tartaric Acid and Aniline.—It was found to be desirable to modify Arppe's method[2] for the preparation of tartranilic acid. Tartaric acid and aniline, in equimolecular proportions, were heated at 140–150°, during 3 or 4 hours. The product was hydrolyzed by warming with an aqueous solution of potassium hydroxide and the anilic acid precipitated from the clear solution by acidification with hydrochloric acid. It is decolorized by means of purified animal charcoal and recrystallized from water. The yield is rather poor.

When treated with amines, tartranilic acid forms salts; in no case was any tendency shown to pass into an imide. *Aniline tartranilate*, prepared at 100°, in alcoholic (50 per cent.) solution, is deposited in colorless crystals, melting at 149–150°. *Quinolinium tartranilate* is prepared in a similar manner; colorless crystals, melting at 129–130°. It is not soluble in ether, but dissolves in water. There can hardly be any doubt that these salts could be prepared at the ordinary temperature if it were desired; we heated their components because of the transformation tests which were being conducted. When treated with hydrochloric acid each salt precipitates tartranilic acid, whereas with an aqueous solution of sodium carbonate the salts liberate aniline and quinoline, respectively. *β-Naphthylamine tartranilate* is prepared from the acid and amine, at the ordinary temperature, in alcoholic solution, and forms colorless crystals, melting at 176–177°. It dissolves readily in hot water, more sparingly in cold water and in alcohol. When mixed with tartranilic acid, the melting point of the salt is lowered considerably.

Water is evolved if the salt is heated at 180°; the residue consists of a *compound* which melts at 240–241° and is also formed from *aniline tartar-β-naphthylamidate*, see below.

Tartaric Acid and β-Naphthylamine.—A number of attempts were made to prepare *tartar-β-naphthylamidic acid*, $C_{10}H_7NHCOCH(OH)CH(OH)CO_2H$. Ultimately it was obtained, in small quantity, by the following process: β-Naphthylamine (1 mol.) and tartaric acid ($1^1/_3$ mols.) were heated at 180–200°, during 3 hours. The powdered product was boiled during 30 minutes with excess of a concentrated aqueous solution of potassium hydroxide, the liquid filtered while hot, then allowed to cool and filtered again. Unless this is done a resin which is present will cause a good deal of trouble by stopping the pores of the filter paper. The clear filtrate is now acidified with hydrochloric acid, which precipitates a black gummy material. This was removed and extracted with boiling water; the solution, when cold, deposits a brown

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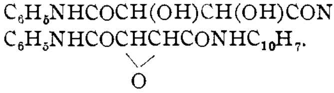
[1] *Ann.*, **77**, 277.

[2] *Ibid.*, **93**, 355.

substance, which was extracted with a hot aqueous solution of potassium hydroxide. The alkaline filtrate was boiled with animal charcoal and the amidic acid precipitated from the clarified liquid by means of hydrochloric acid. Under these circumstances the yield is, of course, quite small, and as our material was not absolutely colorless, we decided to study its reactions and not attempt to purify it further for analysis. The amidic acid melts at about 220° under ordinary circumstances, but when placed in a bath previously heated to 180–185°, the acid melts immediately, evolves water, resolidifies and then melts about 220°. This substance (m. p. 220°) is therefore the *β-naphthylimide.* The amidic acid dissolves readily in an aqueous solution of sodium carbonate and it has an acid reaction towards litmus; it is also soluble in hot water and in alcohol. This latter solution, when mixed with a similar one of aniline (1 mol.), forms the aniline salt; colorless crystals, melting at 172–174°.

This salt evolves water when it is fused and the residue consists of the same *compound* (m. p. 240–241°) which is formed under similar conditions from β-naphthylamine tartranilate (see above). The two materials were identified by a mixed melting point determination. When fully purified the compound is obtained in colorless crystals, melting at 240–242°. It dissolves readily in pyridine, but more sparingly in alcohol and is insoluble in hot water or in an aqueous solution of potassium hydroxide. When melted it does not evolve water nor an amine. Its methods of formation and its properties show that the compound is a *dianilide,* probably, $C_6H_5NHCOCH(OH)CH(OH)CONHC_{10}H_7$, though it might, of course, be the anhydride,

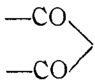


$C_6H_5NHCO\underset{\diagdown O \diagup}{CHCH}CONHC_{10}H_7$.

Summary.

1. The action of various amines on a number of dibasic aliphatic acids, and on the *N*-substituted amidic acids derived from them, has been investigated.

2. The aliphatic amidic acids, RNHCO * * * CO_2H, behave quite differently from the corresponding compounds of the aromatic series.

3. With the aromatic compounds, amines, in general, form *N*-substituted imides,  $\left.\begin{matrix}-CO\\-CO\end{matrix}\right\rangle NR$, whereas with the aliphatic compounds they either fail to react or else they produce well defined salts which are relatively stable.

4. The cause of this difference in behavior appears, at present, to be ascribable only to the inherent nature of the benzene nucleus, whatever that may be.

5. In connection with furmaric and maleic acids, attention may be called to the ease with which aniline adds to the double linkage.

6. We were unable to isolate a dianiline salt from any of the dicarboxylic acids which we investigated.

7. From aniline tartar-β-naphthalamidate and also from β-naphthylamine tartranilate (tartarphenylamidate) we prepared what is probably an unsymmetrical diamide. In this reaction these acids resemble similar compounds in the phthalic series.

8. We have prepared a considerable number of new compounds and we have devised improved methods for obtaining certain other substances.

The work will be continued in this laboratory during the coming academic year.

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THE HYDROLYSIS OF SALICIN BY THE ENZYME EMULSIN.

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Received September 20, 1909.

In aqueous solution salicin is hydrolyzed by strong acids to glucose and salicyl alcohol according to the equation,[1]

$$C_{13}H_{18}O_7 + H_2O = C_6H_{12}O_6 + C_7H_8O_2.$$
$$\text{(Salicin)} + \text{(water)} = \text{(glucose)} + \text{(salicyl alcohol.)}$$

It has been found by A. A. Noyes and Hall[2] that the rate of this acid hydrolysis follows the law of unimolecular reactions. The same hydrolysis can also be accomplished by adding to the salicin solution a little of the enzyme of almonds, called emulsin, but in this case it has been stated by Henri[3] and other investigators that the rate does not follow at all the unimolecular law. As this statement that the enzymotic hydrolysis of salicin by emulsin does not follow the usual laws of chemical dynamics has passed unchallenged for many years it has been widely accepted as correct. Against such a conclusion it is to be said that the glucose which is liberated from salicin by the action of emulsin is doubtless β-glucose because emulsin hydrolyzes only the β-glucosides, and β-glucose has a rotatory power of 20°, but Henri, in his work, assumed that the glucose had its usual specific rotation, 52°. His polariscopic measurements of the rate of the enzymotic hydrolysis are accordingly incorrect, for he made no correction for the mutarotation of glucose. In the hydrolysis by acids, as studied by A. A. Noyes and Hall, this second reaction, the mutarotation of glucose, does not affect the estimation of the extent of the hydrolysis from the polariscopic readings because the strong acid and the high temperature (95°) employed make the rate of the mutarotation instantaneous in comparison with the rate of the hydrolysis, but in the hydrolysis by emulsin the polariscopic readings do not give the real extent of the hydrolysis unless a considerable correction is made for the mutarotation of the freshly liberated glucose. The case is very similar to the hydrolysis of cane sugar by the enzyme invertase, in which reac-

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[1] Piria, *Ann.*, **56**, 37.

[2] *Z. physik. Chem.*, **18**, 240–4 (1895).

[3] *Lois générales de l'action des diastases*, p. 102.