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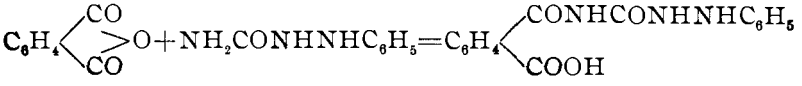
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MICHIGAN.]

THE ACTION OF PHENYLSEMICARBAZIDE AND SEMICARBAZIDE HYDROCHLORIDE ON PHTHALIC ANHYDRIDE.

BY FREDERICK L. DUNLAP.

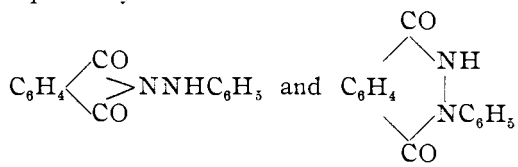
Received July 3, 1905.

WHEN phenylsemicarbazide and phthalic anhydride are heated together to 140-145°, they combine to form phthalic acid monophenylsemicarbazide as follows:



This acid decomposes on heating, carbon dioxide and small quantities of ammonia being at first evolved. As the decomposition proceeds, the amount of carbon dioxide formed gradually

decreases while the amount of ammonia increases. After the decomposition is complete, the resulting melt may be separated, by use of appropriate solvents, into three products, phthalimide, phthalylphenylhydrazine (anilidophthalimide), and 1,4-diketo-2-phenyl-1,2,3-4-tetrahydro-2,3-benzdiazine, the last two products being respectively



Phthalylphenylhydrazine has been described by a number of investigators, and of especial note is the disagreement as to the true color of this compound. Pickel[1], its discoverer, found it to be yellow. The same year that Pickel's work appeared, Hötte,[2] in a preliminary report on the action of phenylhydrazine on the anhydrides of organic acids, makes brief mention of this compound and describes it as being yellow. Pellizzari[3] found it to be straw-colored and says that in crystallizing it from alcohol, "*it can assume rather different aspects, so much so as to make one doubt whether the substance is a single compound (unico).*"[4] Just[5] has obtained this compound by a method exactly similar to Pellizzari's, but he describes it as being colorless.

In 1887, Hötte[6] published the full details of the research, the preliminary report on which had appeared the preceding year. In a foot-note in this paper,[7] he calls attention to the discrepancy in color ascribed to this compound by various investigators, and also states[8] that from alcohol, this substance crystallizes in warty aggregations of needles as well as in longer prismatic crystals. Henriques[9] describes the color as yellow, while Eibner and Merkle[10] say it is colorless. In attempting to purify the phthalylphenylhydrazine, formed during the decomposition of phthalic acid monophenylsemicarbazide, it was found that there were un-

[1] Inaugural Dissertation (Erlangen), p. 12 (1885); *Ann. Chem.* (Liebig), **232**, 232 (1886).
[2] *J. prakt. Chem.* [2], **33**, 99 (1886).
[3] *Gazz.*, **16**, 203 (1886).
[4] *Loc. cit.*, page 204.
[5] *Ber.*, **19**, 1204 (1886).
[6] *J. prakt. Chem.* [2], **35**, 265 (1887).
[7] *Ibid.*, p. 270, foot note No. 4.
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questionably two bodies of different appearance present, which were unlike not only in their color but also in their crystalline habit. Unable to separate them at first by means of solvents, conditions were found under which the crystals could be obtained of sufficient size so that they could be separated mechanically. One form was white, the other being lemon-yellow. Both these compounds had the same melting-point and gave the same results on analysis, and it then became evident that it was a case of physical isomerism that was being dealt with.

A careful study of the conditions showed that the stable or yellow form may be readily produced in a number of ways and quite free from the labile or white form. For example, if a saturated glacial acetic acid solution of this compound is made at the boiling-point of the acetic acid, and then the temperature is allowed to drop a few degrees and held at this point, when crystallization takes place, it is always with the formation of the stable form, quite free from the labile; or, if either the labile or stable, or a mixture of the two, be heated with a boiling saturated solution of phthalylphenylhydrazine in alcohol, acetone, or glacial acetic acid, the undissolved part rapidly and completely passes over into the stable form. Perhaps the most satisfactory method for the production of the labile form is by crystallization from alcohol, although the labile form thus separated is seldom quite free from some of the stable.

When a boiling-hot saturated solution of phthalylphenylhydrazine in acetone is allowed to stand, the crystals separate but slowly and usually both forms are produced in crystals frequently measuring several millimeters in length. The crystals formed in this way were satisfactory for crystallographic measurement, and it has been found that the labile form crystallizes in the orthorhombic system, while the stable is monoclinic. That the two forms have the same melting-point is explained by the fact that the transition temperature of the labile into the stable lies a number of degrees below the melting-point of the stable. No satisfactory melting-point of the labile was obtained even by the dipping method.

The compound previously mentioned as 1,4-diketo-2-phenyl-1,2,3,4-tetrahydro-2,3-benzdiazine, has been previously described by Pellizzari[1] (under the name of phthalyl phenylhydrazide) and

[1] *Gazz.*, **16**, 205 (1886).

by Hötte[1] who calls it β-phthalylphenylhydrazine in contradistinction to the compound $C_6H_4\begin{matrix}CO\\ \\ CO\end{matrix}>NNHC_6H_5$, which he named α-phthalylphenylhydrazine.[2] Both Pellizzari and Hötte describe the β-compound as white, while Henriques[3] says that it is pale red. I have obtained the β-compound many times during the course of this work, and, when perfectly pure, it is always white in color.

The constitution

$$C_6H_4\begin{matrix}CONHCONHNHC_6H_5\\ \\ COOH\end{matrix}$$

has been given to the compound formed by the addition of phthalic anhydride and phenylsemicarbazide, as it best explains the formation of the various decomposition products. In the first place, when the acid is heated to its melting-point, carbon dioxide and a small amount of ammonia are produced. This first stage in the decomposition may be represented as follows:

$$C_6H_4\begin{matrix}CONH\\ \\ CO\end{matrix}\begin{matrix}CO\\ |\\ O\end{matrix}\begin{matrix}NHNHC_6H_5\\ |\\ H\end{matrix} =$$

$$C_6H_4\begin{matrix}CO\\ \\ CO\end{matrix}>NH + CO_2 + C_6H_5NHNH_2,$$

with the formation of phthalimide, carbon dioxide and phenylhydrazine. In the first stages of the decomposition, the odor of phenylhydrazine is distinctly noticeable in the escaping gases. The next stage in the reaction is the action of the phenylhydrazine on the phthalimide:

$$C_6H_4\begin{matrix}CO\\ \\ CO\end{matrix}>NH + NH_2NHC_6H_5 = C_6H_4\begin{matrix}CO\\ \\ CO\end{matrix}>NNHC_6H_5 + NH_3.$$

That such a reaction may take place between phthalimide and phenylhydrazine, has been shown by both Just[4] and Pellizzari,[5] and I have also had occasion to verify it many times. This

[1] *J. prakt. Chem* [2], **35**, 281, 284, 290 (1887).

[2] For the sake of brevity, Hötte's nomenclature with respect to these compounds will be made use of.

[3] *Ber.*, **21**, 1617 (1888).

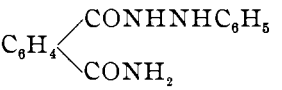
[4] *Ibid.*, **19**, 1204 (1886).

[5] *Gazz.*, **16**, 203 (1886).

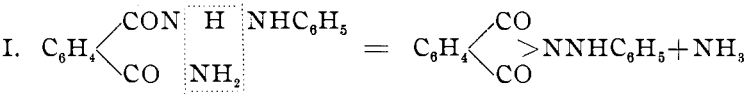
second stage then accounts for the evolution of ammonia, and its increase as the carbon dioxide decreases, it being the later or secondary stage in the decomposition. The loss of some phenylhydrazine during the decomposition of the phthalic acid monophenylsemicarbazide, leaves the phthalimide in excess of the theoretical amount necessary to combine with the phenylhydrazine. N. phenylhydrazine has been isolated from the final product, but phthalimide was readily obtained and identified by its physical properties as well as by analysis. There is still, however, one phase of this reaction to be accounted for, namely, the formation of the β-compound.

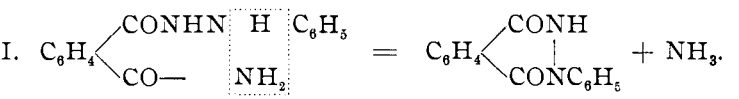
Both Just and Pellizzari in their work on the action of phenylhydrazine on phthalimide, isolated only the α-compound, yet, if the explanation of the decomposition of phthalic acid monophenylsemicarbazide as given above be correct, the only conceivable opportunity for the β-compound to form would be through the interaction of the phenylhydrazine and the phthalimide.

The work of Just and Pellizzari has been carefully repeated, and a ready explanation for the formation of the β-compound was obtained. The first stage in the interaction of these two substances is their addition with the formation of anilidophthaldiamide,



On heating, this compound readily decomposes, the decomposition taking place in two ways:





The first method of decomposition yields the α, while the second produces the β. The α is not formed from the β, or *vice versa*, by molecular rearrangement. The decomposition takes place mainly according to I, the β-compound always forming in smaller amounts, but both products are always formed. The constitution

assigned to phthalic acid monophenylsemicarbazide therefore explains satisfactorily all the facts obtained from the decomposition of this acid.

In studying the action of phenylhydrazine on phthalic anhydride, Pellizzari[1] obtained β-phthalylphenylhydrazine. The accuracy of Pellizzari's work was questioned by Hötte[2], for he isolated only the α-compound. In answer to Hötte, Pellizzari[3] showed that both products were formed in amounts which varied with the reacting masses and the conditions, the β-compound being often formed in great excess. The formation of both the α and β in this fashion suggested a probable similarity to the reactions that I have found when phthalimide and phenylhydrazine interact. In fact, a complete parallelism exists between the two sets of reactions. In the case of the phthalic anhydride and the phenylhydrazine, the first phase is the addition of the two with the formation of anilidophthalamic acid:

$$C_6H_4\begin{cases}CO\\ \\CO\end{cases}>O + NH_2NHC_6H_5 = C_6H_4\begin{cases}CONHNHC_6H_5\\ \\COOH\end{cases}$$

Anilidophthalamic acid is readily decomposed by heat, the decomposition taking place in two ways, with the formation of both α- and β-phthalylphenylhydrazine.

Semicarbazide hydrochloride and phthalic anhydride react readily when subjected to heat, with the formation of phthalylsemicarbazide:

$$C_6H_4\begin{cases}CO\\ \\CO\end{cases}>O + NH_2CONHNH_2.HCl =$$

$$C_6H_4\begin{cases}CO\\ \\CO\end{cases}>NCONHNH_2 + H_2O + HCl.$$

Phthalylsemicarbazide is readily soluble in dilute alkali, and on acidifying this solution phthalic acid monosemicarbazide precipitates:

$$C_6H_4\begin{cases}CO\\ \\CO\end{cases}>NCONHNH_2 + KOH = C_6H_4\begin{cases}CONHCONHNH_2\\ \\COOK\end{cases}$$

[1] *Gazz.*, **16**, 205 (1886).
[2] *J. prakt. Chem.* [2], **35**, 270 (1887).
[3] *Gazz.*, **17**, 278 (1887).

$$C_6H_4\begin{cases}CONHCONHNH_2\\COOK\end{cases} + HCl = C_6H_4\begin{cases}CONHCONHNH_2\\COOH\end{cases}$$

The formulae ascribed to these semicarbazide derivatives is based on the assumption that semicarbazide hydrochloride acts similarly to phenylsemicarbazide, yet the question can not be settled beyond peradventure until a thorough study has been made of their decomposition products. That the formula given to the phthalic acid monosemicarbazide is more likely to be correct than the following,

$$C_6H_4\begin{cases}CONHNHCONH_2\\COOH\end{cases},$$

is shown by the fact that a solution of this acid is not oxidized in the least even after two hours boiling with mercuric oxide. If the latter formula were correct, we should expect the formation of an azo body.

Experimental Work.

Action of phenylsemicarbazide on phthalic anhydride.

When phenylsemicarbazide and phthalic anhydride are thoroughly mixed in equimolecular proportions, and this mixture heated in a flask in an oil-bath, as the temperature rises, the mass gradually melts and at about 140-145°, the contents of the flask are completely fluid. If the bath is held at this temperature for a few minutes, and the contents of the flask stirred with a glass rod, it soon becomes pasty and then completely solidifies to a light yellow mass. This product was purified by crystallization from glacial acetic acid, from which, however, it deposits with extreme slowness in small white clusters of microscopic needles. This product is slightly soluble in alcohol and water, but is practically insoluble in all the other ordinary solvents. On heating, this substance turns yellow before fusion takes place; it melts at 191-192° with evolution of gas, the melt being of a yellow color.

On analysis, this substance proved to be phthalic acid monophenylsemicarbazide, $C_6H_4\begin{cases}CONHCONHNHC_6H_5\\COOH\end{cases}$

	Calculated for $C_{15}H_{13}N_3O_4$.	Found.
Nitrogen	14.04	14.53

If during the preparation of this substance, after the mass has solidified, the temperature of the bath be raised, at 180-185° the mass softens and becomes a deeper yellow and finally liquefies with vigorous evolution of gas. The gas given off at first is primarily carbon dioxide containing some ammonia, but as the gas evolution proceeds, the carbon dioxide decreases in amount while the amount of ammonia increases. During the early stages of the decomposition, phenylhydrazine is plainly discernible in the escaping gases. After heating for a half hour at 180-185°, the gas evolution practically ceases and the decomposition is complete. After cooling, the contents of the flask were crystallized from alcohol. The first crop of crystals (A) was filtered and the mother-liquor concentrated. On standing, this concentrated mother-liquor deposited another crop of crystals (B). The filtrate from B, on further concentration, deposited still a third crop (C). Fractions A and B were purified by repeated crystallization from alcohol.

Fraction A crystallized from alcohol in white needle-like crystals having a melting-point of 229°. Its melting-point, crystalline form and analysis showed that the product A was phthalimide.

	Calculated for $C_8H_5O_2N$.	Found. I.	Found. II.
Carbon	65.3	65.0	...
Hydrogen	3.4	3.8	...
Nitrogen	9.5	..	9.8

Product C was likewise purified from alcohol after treating with cold alkali, filtering from the insoluble portion, and reprecipitation with acids. It deposited from alcohol in small white prisms having a melting-point of 210°. This product was identified as 1,4-diketo-2-phenyl-1,2,3,4-tetrahydro-2,3-benzdiazine. On analysis, the following results were obtained:

	Calculated for $C_{14}H_{10}O_2N_2$.	Found. I.	Found. II.	Found. III.
Carbon	70.58	70.28	...	...
Hydrogen	4.2	4.47	...	...
Nitrogen	11.76	...	12.27	12.18

Product B was only small in amount and in attempting to purify it by crystallization from glacial acetic acid, it was noticed that the product invariably separated in two forms, one lemon-yellow, the other white in color. Glacial acetic acid, while an

excellent medium from which to crystallize this substance, did not seem able to effect a separation of the two, so that the two forms were finally separated by hand, a comparatively simple task, as the crystals were of good size. The lemon-yellow crystals on analysis gave the following results:

	Calculated for $C_{14}H_{10}O_2N_2$.	Found. I.	II.	III.	IV.
Carbon	70.58	71.36	71.22	...	...
Hydrogen	4.2	4.45	4.6	...	...
Nitrogen	11.76	...	...	11.88	11.85

The white crystals gave the following results on analysis:

	Calculated for $C_{14}H_{10}O_2N_2$.	Found. I.	II.	III.
Carbon	70.58	70.30	...	...
Hydrogen	4.2	4.14	...	...
Nitrogen	11.76	...	12.26	12.16

These two sets of analyses made it evident that the substances dealt with were of the same percentage composition. The lemon-yellow substance melted at 179-179.5°, while the white body on heating in a melting-point tube, turned yellow before melting and then showed the same melting-point as the lemon-yellow substance. The analyses and the question of the melting-point showed that these two substances were either stereochemical or physical isomers. Further study of this question showed that it was a case of physical isomerism. The two substances analyzed were phthalylphenylhydrazine, $C_6H_4\begin{matrix}CO\\ \\ CO\end{matrix}>NNHC_6H_5$.

With respect to this compound, it is interesting to note that both Pickel and Hötte state that when warmed with concentrated sulphuric acid, a wine-red or violet color is produced. I have never succeeded in obtaining anything but the faintest suggestion of a violet color, just visible against the white background of an evaporating dish. However, if a trace of an oxidizing agent is added, an intense violet color is developed. That is, this compound gives the Bülow reaction with great sharpness. Doubtless both Pickel and Hötte worked with sulphuric acid containing more or less nitric acid. The reaction is very sensitive and may be used to detect nitric or other oxidizing agents in sulphuric acid. Pellizzari has noted the fact that this compound gives an intense color with nitric and sulphuric acids.

PREPARATION OF THE STABLE FORM OF $C_{14}H_{10}N_2O_2$.

The phthalylphenylhydrazine used in these experiments as well as those on the labile modification, was prepared by the methods of both Just[1] and Hötte,[2] except that the temperature was raised until the mixtures were fluid, and then held at this point until the gas evolution had ceased. The product obtained was, in both cases, ground until quite fine and then treated with dilute alkali to remove all the β-isomer present.

The following method has proved the most satisfactory in preparing considerable amounts of the yellow or stable modification: Dissolve phthalylphenylhydrazine in boiling glacial acetic acid and continue the addition of the solid until the solution is about saturated. Lower the flame under the boiling solution and allow the temperature to fall very slowly. In about an hour, the liquid will have deposited bright lemon-yellow crystals which may be readily separated from the hot mother-liquor by decantation. The crystals remaining in the flask should then be rapidly washed twice with fresh portions of glacial acetic acid and then finally dried between folds of filter-paper. Prepared in this way, the stable modification may be obtained quite free from the labile. This modification on analysis gave the following results:

	Calculated for $C_{14}H_{10}O_2N_2$.	Found.
Nitrogen.....	11.76	12.07

PREPARATION OF THE LABILE FORM OF $C_{14}H_{10}O_2N_2$.

Perhaps the simplest method for the preparation of this modification, is to heat phthalylphenylhydrazine until it becomes thoroughly fluid, and then cool rapidly. The cooled mass is usually a yellow varnish-like mass, which, on flooding with alcohol, immediately begins to crystallize in the colorless labile form. The production of the labile modification by crystallization from solvents, especially if *complete* absence of the other modification is looked for, is rather uncertain of accomplishment. Many experiments have been carried out with various solvents under different conditions of concentration, temperature, etc., but no condition was found that was absolutely certain to produce the labile form quite free from the stable every time the experiment was repeated. Microscopic examination of the colorless

[1] *Ber.*, **19**, 1254 (1886).

[2] *J. prakt. Chem.* [2], **35**, 268 (1887).

Fig. I.

form almost invariably showed traces of the yellow modification. Reference should be made to two cases which frequently gave excellent results, *i. e.*, produced the white modification with but very small amounts of the other. In one case, a quite concentrated and hot glacial acetic acid solution of phthalylphenylhydrazine was placed in boiling-hot water in a beaker which was thoroughly insulated with hair felt, in consequence of which the temperature of the solvent dropped quite slowly. In this case, the labile modification separated practically free from the yellow, except at the bottom of the tube in which the crystallization took place. Again, the white modification has been obtained frequently from an alcoholic solution, especially when the solution had stood quietly and had reached room temperature before crystallization took place. It must, however, be borne in mind, that absolute certainty as to the results are not to be expected from these two methods. A sample of the white modification prepared by the use of glacial acetic acid as a solvent, gave the following results on analysis:

	Calculated for $C_{14}H_{10}O_2N_2$.	Found.
Nitrogen.....	11.76	12.09

Ordinarily, from such solvents as glacial acetic acid, benzene, alcohol, acetone, etc., both forms appear together. Solutions of both the white and yellow modifications are yellow.

The above figure shows both forms together. The magnification is twenty-five diameters. This preparation was made by heating phthalylphenylhydrazine on a microscope slide until the solid had become quite liquid. By means of a warm platinum spatula, the fluid was spread out over the slide in a thin layer, and then immediately dropped on the surface of a mercury bath in order to cool the slide rapidly. When cold, the slide was found covered with a thin layer of a yellow varnish-like mass, which, on flooding with alcohol, immediately began to separate the white modification in the form of minute crystals. The slide was then carefully heated at one point in order to convert the white into the yellow form. With care, this conversion may be accomplished without fusing the labile form. In the above figure, the feathery fringe of crystals are the white, while the heavier and more compact masses are the yellow modification. Under the microscope, the distinction in color between these two is most marked.

The transition temperature of the labile into the stable form was not determined, although it was observed that five hours' heating in a Victor Meyer bath at 95° did not effect any change, but at 150°, the conversion is complete in a very few minutes. In the latter case, the temperature of the bath was controlled by boiling anisol (b. p. 155°).

The best method for obtaining both these forms in characteristic crystals, is to crystallize slowly from hot acetone. When such a solution is placed in a shallow layer in a crystallizing dish and allowed to cool spontaneously, it frequently is a matter of many hours before crystallization takes place. Both forms usually occur together, but the crystals are of such a size that they may be readily separated by hand. I am indebted to Professor E. H. Kraus of this University for the following observations as to the crystallographic development of these modifications, the crystals measured being obtained from acetone.

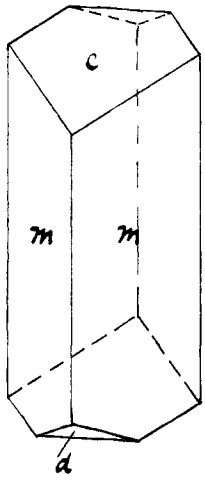


Fig. 2.

YELLOW MODIFICATION.

The crystals of this modification (Fig. 2) were clear, transparent, distinctly yellow in color, and about 2 to 5 mm. in length. The usual combination, as shown by Fig. 2, consists of the unit prism, $m\ \{110\}$, the basal pinacoid, $c\ \{001\}$, and the positive hemiorthodome, $d\ \{\bar{1}01\}$. The habitus is generally prismatic in that the unit prism predominates. The measurements are as follows:

CRYSTAL SYSTEM: MONOCLINIC, HOLOHEDRAL.

$a:b:c = 1.1671:1:0.7848.$

$\beta = 54° 50'.$

	Observed.	Calculated.
$110 : \bar{1}10 =$	87° 18′	.....
$\bar{1}10 . \bar{1}01 =$	85° 8′	. ....
$110 : 001 =$	65° 22′	.....
$001 : \bar{1}01 =$	42° 6′	41° 54′

A very perfect cleavage parallel to the faces of the unit prism, $m\ \{110\}$, was noted.

WHITE MODIFICATION.

These crystals are colorless and transparent, and usually 2 to 3 mm. in length and about 1 mm. in thickness. Fig. 3 shows the

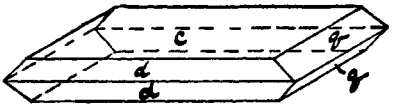


Fig. 3.

usual combination of forms and consists of the basal pinacoid, $c\ \{001\}$, the macrodome, $d\ \{101\}$, and the brachydome, $q\ \{011\}$. The basal pinacoid usually predominates, which gives the crystals a tabular habitus. Inasmuch as most of these forms give quite good signals, the measurements are, for the most part, to be considered as accurate. The measurements are as follows:

CRYSTAL SYSTEM: ORTHORHOMBIC, HOLOHEDRAL.

$a:b:c = 0.2526:1:0.9118.$

	Observed.	Calculated.
001 : 011 =	42° 21½′	.....
001 : 101 =	74° 31′	.....
101 : 011 =	78° 38′	78° 43′

A perfect cleavage parallel to the basal pinacoid, $c\ \{001\}$, was noted.

THE ACTION OF PHENYLHYDRAZINE ON PHTHALIMIDE.

Equimolecular quantities of phthalimide and phenylhydrazine were heated together in a flask immersed in an oil-bath, the temperature of the bath being gradually raised until it registered 120°. During this operation, the mixture was constantly stirred with a glass rod. As the temperature increased, the mass assumed a yellow color and ammonia was given off. In a few minutes the mass solidified. It was then ground fine and washed with cold alcohol, a pure white product being obtained by this treatment. After being crystallized from alcohol, the substance was submitted to analysis with the following results:

	Calculated for $C_{14}H_{18}N_8O_2$.	Found. I.	II.	III.
Nitrogen.....	16.47	17.52	17.58	17.34

While the analyses are not as close as could be wished for, yet they show that the substance is anilidophthaldiamide. This substance is so readily decomposed that although numerous

methods of purification were tried, none gave any better results than simple crystallization from alcohol, the hot alcoholic solution, however, being rapidly cooled in ice water. Hötte[1] also obtained this compound during the course of his work, and likewise found it sufficiently unstable and difficult of purification, so that accurate analytical figures were not obtainable. The method of preparation used by Hötte in making this substance, was that of treating phthalylphenylhydrazine with alcoholic ammonia. He gives its melting-point as 146°, but I was unable to obtain a satisfactory melting-point as the substance decomposes so readily, figures being obtained from 156-185°, but none of them so low as that given by Hötte. Melting was always accompanied by evolution of gas and the conversion of the compound into a yellow substance.

It is worthy of notice that even during the solution of the anilidophthaldiamide in alcohol with the aid of heat, decomposition takes place to such an extent that it is comparatively easy to show the presence of both α- and β-phthalylphenylhydrazine in the solution.

Anilidophthaldiamide crystallizes from alcohol in very small colorless flat prisms. This substance is soluble in hot acetone and glacial acetic acid, but less soluble in ethyl acetate. In all other of the ordinary solvents, this compound is practically insoluble.

The ease with which phenylhydrazine and phthalimide combine is seen by the fact that if they are mixed in equimolecular proportions and allowed to stand at ordinary temperatures, in a few hours the odor of ammonia is easily detected, and, in a day or two, the mixture has set to a dense solid mass of anilidophthaldiamide,

DECOMPOSITION OF ANILIDOPHTHALDIAMIDE BY HEAT.

In carrying out this work, experiments have been made with the purest anilidophthaldiamide I have been able to prepare, as well as with the crude product without purification. The results were the same in both cases. If phenylhydrazine and phthalimide are heated together to 120° and stirred until the mass becomes solid, the resultant crude anilidophthaldiamide may be readily decomposed by carrying the temperature still higher. If the temperature of the bath in which the mass is being heated is carried up to 140°, the solid mass again liquefies and ammonia is evolved

[1] *J. prakt. Chem.* [2], **35**, 280 (1887).

in great quantities. Fifteen minutes is usually a sufficient length of time to heat the mixture in order to bring the decomposition to an end. The resultant product was crystallized from alcohol, the product which separated being practically pure α-phthalylphenylhydrazine, as was easily shown by the melting-point, and presence in the two isomeric forms. The filtrate from this crop of crystals was evaporated to a very small bulk, and, after standing for some time, the crystals which separated were thoroughly ground and treated with dilute alkali. The alkaline solution, after acidifying, deposited a white precipitate which was filtered off and crystallized from alcohol. This product had the melting-point of 210° and was readily identified as β-phthalylphenylhydrazine. The portion insoluble in the dilute alkali was the α isomer.

THE ACTION OF PHENYLHYDRAZINE ON PHTHALIC ANHYDRIDE.

Equimolecular quantities of these two substances were dissolved separately in chloroform and the solutions then mixed. The mixture became warm and shortly began to separate a white crystalline product. After standing for several hours, this was filtered and washed with a little chloroform. After crystallization from alcohol, this substance gave the following results:

	Calculated for $C_{14}H_{12}O_3N_2$.	Found.
Nitrogen.....	10.93	10.90

The above analysis identified the body as anilidophthalamic acid.

The yield was about 65 per cent. of the theory and the acid was practically pure without crystallization from alcohol. It is rather easily decomposed, an alcoholic solution of it darkening slowly when boiled. The melting-point was uncertain and could not be satisfactorily determined on account of the ease with which the acid decomposes. Hötte gives it as 165-166° and Pellizzari as 163°, but while attempts have been made many times to get satisfactory duplicate melting-points, yet I have been unable to obtain them. This method for the preparation of this addition product is greatly superior to the method of Hötte, being very much more rapid and the product much purer.

DECOMPOSITION OF ANILIDOPHTHALAMIC ACID BY HEAT.

The pure acid was heated until fused and the gas evolution which took place on melting had ceased. The resulting product

was treated exactly as described above with respect to the product obtained by heating anilidophthaldiamide. Furthermore, the decomposition products isolated were the same, namely, both α- and β-phthalylphenylhydrazine.

In the decomposition of the anilidophthalamic acid, the relative proportions of the α- and β-bodies formed, depends on the temperature at which the decomposition takes place. Two experiments will show this clearly:

(1) The acid was placed in a small Erlenmeyer flask and heated in an oil-bath until the bath registered 160-170°. In a few minutes the mass had completely liquefied and the gas evolution had ceased. The decomposition product was removed from the flask and the β-isomer separated from the α by its solubility in alkali. The result showed that the decomposition product was composed of 20 per cent. of the β and 80 per cent. of the α.

(2) A flask was heated in an oil-bath until the bath registered 210°. The acid was introduced then in small portions, each portion having completely melted and the gas evolution ceased before a fresh lot of acid was added. The decomposition product was separated into its constituents as in the previous experiment, and it was found that there had been formed 40 per cent. of the β-isomer and 60 per cent. of the α isomer.

ACTION OF SEMICARBAZIDE HYDROCHLORIDE ON PHTHALIC ANHYDRIDE.

When equimolecular quantities of semicarbazide hydrochloride and phthalic anhydride are intimately mixed and heated in a flask in an oil-bath, when the bath registers about 150°, the mixture is a soft and pasty mass. At 160°, hydrochloric acid is freely evolved. The temperature was held at 160° for one hour, at the expiration of which time, the hydrochloric acid had practically ceased being evolved. Occasionally, the mass will solidify at this elevated temperature when stirred with a glass rod. The cooled mass was then crystallized from glacial acetic acid, from which it separates in white needles. The pure product is slightly soluble in boiling water and alcohol, but insoluble in the other solvents. It melts at about 262° with gas evolution, the melt being yellow. On analysis, the following results were obtained:

	Calculated for $C_9H_7O_3N_3$.	Found. I.	II.	III.
Nitrogen.....	20.48	20.47	20.35	20.75

Phthalylsemicarbazide dissolves readily in cold alkalies, momentarily turning yellow. When this solution is acidified, a white crystalline precipitate is obtained, which is readily purified by crystallization from water, in which it is readily soluble and from which it separates in slender, white prisms. This product is soluble in alcohol and glacial acetic acid, but insoluble in ether, chloroform and benzene.

This substance, like phthalylsemicarbazide, melts at about 262°, with gas evolution, the melt being yellow. That this phthalic acid monsemicarbazide has the same melting-point as the phthalylsemicarbazide, is due to the fact that the former is converted into the latter before fusion takes place.

On analysis, the following results were obtained:

	Calculated for $C_9H_9O_4N_3$.	Found. I.	Found. II.
Carbon	48.43	48.72	...
Hydrogen	4.04	4.28	...
Nitrogen	18.83	...	18.84

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE NEBRASKA WESLEYAN UNIVERSITY.]

THE BENZALDEHYDE-AZO-BENZOIC ACIDS.

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THE ISOMERIC *m*- and *p*-azoxybenzaldehydes and many of their derivatives were described by one of us[1] three years ago, it being stated[2] at the time that when *p*-azoxybenzaldehyde is heated with concentrated sulphuric acid to 110° to 120° it is changed into a brown substance, which shows the characteristic properties of the oxyazo compounds. Since then Human and Weil[3] in several publications have contended that, instead of the change indicated above taking place, the two azoxybenzaldehydes when heated with concentrated sulphuric acid, pass into the isomeric benzaldehydeazobenzoic acids, as represented by the following equations:

[1] *Am. Chem. J.*, **28**, 34, 475.
[2] *Ibid.*, **28**, 476.
[3] *Ber.*, **36**, 3469, 3801; Human: Inaugural Dissertation, Univ. of Basel, 1904.