

The average of error between the two methods is scarcely greater in any case than would be likely to occur in ordinary duplicate analyses. Certainly the above results do not indicate that 0.2 per cent. should be deducted from all hot water digestions to give the correct data, as was maintained to the writer last winter by a German sugar chemist.

#### THE RICHEST PORTION OF THE BEET.

In answer to many inquiries some analyses were made tending to show what portion of the beet has the greatest sugar content. The samples were all carefully topped at the leaf line, thoroughly brushed and divided horizontally into approximately three equal portions. The samples were grated by hand, carefully mixed and analyzed by the hot water digestion method. The results are given in the following table :

No. of sample.	Upper portion of beet. Per cent. sugar.	Middle portion of beet. Per cent. sugar.	Lower portion. of beet. Per cent. sugar.
1 .....	11.20	13.20	13.50
2 .....	11.60	12.30	11.60
3 .....	9.93	9.98	9.73
4 .....	11.16	13.64	12.87
5 .....	11.70	13.90	10.80
6 .....	10.10	11.30	10.30
7 .....	11.60	12.10	14.20
8 .....	9.10	10.40	11.10
9 .....	10.50	12.40	10.10
10 .....	11.08	13.2	13.00
Average .....	10.9	12.2	11.7

Where only *portions* of beets are used to make up the sample for analysis, a full-length longitudinal section should be taken, and the same fractional portion of each beet.

[CONTRIBUTIONS FROM THE SHEFFIELD LABORATORY OF YALE UNIVERSITY.]

### ON THIOUREAAMIDINES : A CORRECTION.

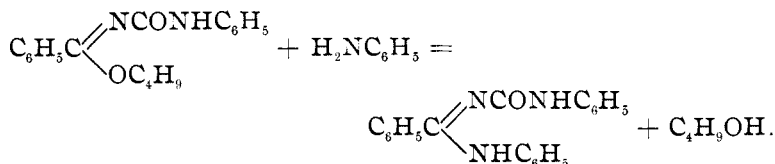
BY HENRY L. WHEELER.

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RECENTLY Wheeler and Sanders<sup>1</sup> published an article on ureaimido esters, thioureaimido esters, acylthioureaimido esters and ureaamidines. An examination of the behavior of the ureaimido esters towards organic bases showed that they reacted

<sup>1</sup> This Journal, 22, 365.

in every case. For example, phenylureaimidoisobutyl benzoate and aniline reacted as follows :



In other words this ureaimido ester behaved in the normal manner with aniline, and an amidine was formed, as was shown by analysis. That this is correct has now been thoroughly established by the preparation of the above ureaamidine from benzenylphenylamidine<sup>1</sup> and phenyl isocyanate.

When the corresponding thioureaaimido esters and acylthioureaaimido esters were treated with aniline,  $\beta$ -naphthylamine, *p*-anisidine, etc., products were obtained which from analogy were assumed by the writer to be thioureaamidines, although in the five cases described the determinations of nitrogen invariably came low. It was at that time thought that these results were due to the fact that the compounds burn with great difficulty.<sup>2</sup>

After the above was published it was found that our analytical results agreed better with those calculated for the corresponding thiourea derivatives (column B, below) than with those of the supposed thioureaamidines (column A). The thiourea derivatives have now been prepared, and a comparison of these with our so-called thioureaamidines shows that the compounds are identical.

The following correction is therefore to be made in our work :

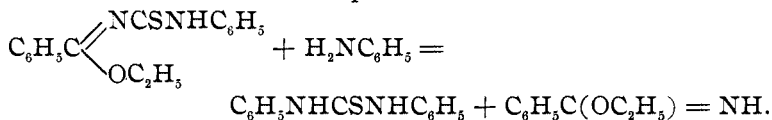
A.	B.
Benzenylphenylthiourea- <i>p</i> -anisylamidine . . . .	phenyl- <i>p</i> -anisylthiourea.
Benzenylphenylthiourea-phenylamidine . . . . .	diphenylthiourea.
Benzenylphenylthiourea- $\beta$ -naphthylamidine . . . .	phenyl- $\beta$ -naphthylthiourea.
Benzenylbenzoylthiourea-phenylamidine . . . . .	benzoylphenylthiourea.
Benzenylbenzoylthiourea- <i>o</i> -tolylamidine . . . . .	benzoyl- <i>o</i> -tolylthiourea.

It has also been found that the true thioureaamidines are decidedly different from our previously described products. Two examples of these have been prepared by combining benzenylphenylamidine with phenyl mustard oil and benzoylrhodanide, respectively. The action of organic bases on the thioureaaimido esters,

<sup>1</sup> Prepared by Pechmann's method: *Ber. d. chem. Ges.*, **30**, 1782 (1897).

<sup>2</sup> For an example of such a case, see benzoyl-*m*-chlorphenylurea and the corresponding thiourea. Wheeler and Johnson: *Am. Chem. J.*, **24**, 220 (1900).

therefore, proceeds as follows, giving a thiourea derivative and an imido ester or its reaction products :



The reaction is unique inasmuch as it differs from that of both oxygen analogues and acylimido esters.<sup>1</sup> It may also be added that phenylthioureaaimidoisobutyl benzoate gave phenylthiourea with aqueous-alcoholic ammonia ; and that benzoylthiourea was obtained from benzoylthioureaaimidomethylphenyl acetate and phenylhydrazine.<sup>2</sup>

## EXPERIMENTAL PART.

*Benzenylphenylureaphenylamidine*,  $\text{C}_6\text{H}_5\text{C} \begin{array}{l} \diagup \text{NCONHC}_6\text{H}_5 \\ \diagdown \text{NHC}_6\text{H}_5 \end{array}$ , was

prepared by dissolving 2 grams of benzenylphenylamidine in benzene and adding the calculated quantity of phenyl isocyanate (1.2 grams), whereupon the ureaamidine separated at once. It was found to be difficultly soluble in alcohol, more readily in benzene, from which solutions it separated in the form of fine needles melting sharply from 179°–180°. It was identical in appearance and properties with the product obtained from phenylureaimidoisobutyl benzoate and aniline.

*Benzenylphenylthioureaaphenylamidine*,  $\text{C}_6\text{H}_5\text{C} \begin{array}{l} \diagup \text{NCSNHC}_6\text{H}_5 \\ \diagdown \text{NHC}_6\text{H}_5 \end{array}$  —

Two grams of benzenylphenylamidine and 1.3 grams of phenyl mustard oil were mixed, and fused on the water-bath. On warming for a few minutes, the mixture solidified. It was then crystallized from benzene, whereupon fine needles or prisms separated, melting at 138°. This material had neither the appearance nor properties of the substance previously described under this name. A nitrogen determination gave :

	Calculated for $\text{C}_{20}\text{H}_{17}\text{N}_3\text{S}$ .	Found.
Nitrogen.....	12.68	12.60

*Phenylthioureaaimidoisobutyl Benzoate and Aniline* gave a product crystallizing from alcohol in plates which melted at 151°–152°.<sup>3</sup>

<sup>1</sup> Wheeler and Walden : *Am. Chem. J.*, 20, 568, (1898).

<sup>2</sup> *Loc. cit.*

<sup>3</sup> *Loc. cit.*

A specimen of Kahlbaum's thiocarbanilide had the same appearance and properties, and when a portion was mixed with this material the melting-point was not altered.

	Calculated for $C_6H_5C(NHC_6H_5)=NCSNHC_6H_5$ $C_{20}H_{17}N_2S$ .	Calculated for $C_6H_5NHC_6H_5NHC_6H_5$ $C_{13}H_{12}N_2S$ .	Found.
Nitrogen ..	12.6	12.2	12.0

This material is therefore diphenylthiourea.

*Phenylthioureamidomethyl Benzoate and Paraanisidine* gave a product which, when crystallized from alcohol and amyl acetate, melted at about  $180^\circ$ .<sup>1</sup> On mixing phenyl mustard oil and *p*-anisidine, the compounds combined with evolution of heat. When the white mass, thus formed, was crystallized from amyl acetate it melted at  $170^\circ$ ; on crystallizing then from alcohol it melted at about  $180^\circ$  and seemed to be identical in every respect with the compound previously obtained from the ureaimido ester and *p*-anisidine. An analysis of the substance obtained in the latter manner gave:

	Calculated for $C_7H_5C(NHC_6H_4OCH_3)=NCSNHC_6H_5$ $C_{21}H_{15}ON_2S$ .	Calculated for $C_7H_5NHC_6H_4OCH_3$ $C_{14}H_{13}ON_2S$ .	Found.
Nitrogen .....	11.6	10.8	10.1

The substance is therefore phenyl-*p*-anisylthiourea, possibly mixed with some dianisylthiourea<sup>2</sup> which melts at  $185^\circ$  and contains 9.7 per cent. of nitrogen, and which may result on repeated crystallizations of the mixed thiourea.

*Phenylthioureamidoisobutyl Benzoate and  $\beta$ -Naphthylamine* gave a compound which, when crystallized from alcohol and amyl acetate, formed minute plates, and melted, not sharply, at  $182^\circ$ – $183^\circ$ . This compound should be phenyl- $\beta$ -naphthylthiourea, which, Mainzer<sup>3</sup> states, melts from  $155^\circ$ – $157^\circ$ , but which melts higher on repeated crystallizations, apparently undergoing decomposition. According to Freund and Wolf<sup>4</sup> it melts at  $165^\circ$ . I have found that when phenyl mustard oil and  $\beta$ -naphthylamine are mixed and the product crystallized once from amyl acetate it melts at  $177^\circ$ – $182^\circ$ . On boiling this product with alcohol it melted, not sharply, from  $182^\circ$ – $183^\circ$ , and agreed in all its properties with the material obtained from the thioureamido ester and  $\beta$ -naphthylamine. When the two specimens were mixed no change in melt-

<sup>1</sup> *Loc. cit.*

<sup>2</sup> Salkowski: *Ber. d. chem. Ges.*, 7, 1012 (1874).

<sup>3</sup> *Ber. d. chem. Ges.*, 15, 1417 (1882).

<sup>4</sup> *Ber. d. chem. Ges.*, 25, 1468 (1892).

ing-point was observed. The result of our previous analysis follows :

	Calculated for $C_6H_5C(NHC_{10}H_7)=NCSNHC_6H_5$ $C_{24}H_{19}N_3S$ .	Calculated for $C_6H_5NHCSNHC_{10}H_7$ $C_{17}H_{14}N_2S$ .	Found.
Nitrogen . . . . .	11.0	10.0	10.0

This material is therefore phenyl- $\beta$ -naphthylthiourea.

*Benzoylthiourea*imidoisobutyl Benzoate and Aniline gave a product melting from  $145^\circ$ – $146^\circ$ . This is identical with benzoylphenylthiourea described by Miquel,<sup>1</sup> as melting at  $148^\circ$ – $149^\circ$ . Our previous analysis is appended :

	Calculated for $C_6H_5C(NHC_6H_5)=NCSNHCOC_6H_5$ $C_{21}H_{17}ON_2S$ .	Calculated for $C_6H_5NHCSNHCOC_6H_5$ $C_{14}H_{12}ON_2S$ .	Found.
Nitrogen . . . . .	11.6	10.9	11.2

When benzenylphenylamidine was mixed, either dry or in benzene solution, with benzoylrhodanide, a small amount of well crystallized material, melting at about  $162^\circ$  was obtained, in addition to some varnish. As the properties of these products had nothing in common with those of the above compound, the mixture was not further examined.

*Benzoylthiourea*imidoisobutyl Benzoate and *o*-Toluidine were stated to react, giving a product melting from  $116^\circ$ – $117^\circ$ . The same product has now been prepared from benzoylrhodanide and orthotoluidine, which, as Dixon<sup>2</sup> states, melts at  $118$ – $119^\circ$ . On mixing this with our material the melting-point was not altered. Our former analysis is annexed :

	Calculated for $C_6H_5C(NHC_6H_4CH_3)=NCSNHCOC_6H_5$ $C_{22}H_{19}ON_2S$ .	Calculated for $C_6H_5CONHCSNHC_6H_4CH_3$ $C_{15}H_{14}ON_2S$ .	Found.
Nitrogen . . . . .	11.2	10.3	10.8

NEW HAVEN, CONNECTICUT,  
February 8, 1901.

## A SPECIAL CRUCIBLE FOR CARBON COMBUSTIONS.

BY PORTER W. SHIMER.

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IT may, perhaps, be remembered that in a former paper by the writer on "Carbon Combustions in a Platinum Crucible,"<sup>3</sup> the crucible was cooled externally by means of wet wick in contact with its upper part, drawing its supply of water from a circular trough kept full by the overflow from a hollow stopper.

<sup>1</sup> *Ann. Chem.* (Liebig), [5], 11, 313.

<sup>2</sup> *J. Chem. Soc.* (London), 55, 622.

<sup>3</sup> This Journal, 21, 557, July, 1899.