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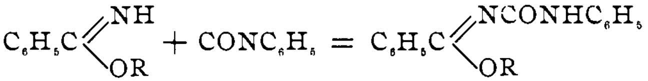
ON UREAIMIDO ESTERS, THIOUREAIMIDO ESTERS, ACYLTHIOUREAIMIDO ESTERS, AND UREAAMIDINES.

[PRELIMINARY PAPER.]

BY HENRY L. WHEELER AND W. MURRAY SANDERS.

REPRESENTATIVES of new classes of compounds, isomeric or metameric with the acylpseudourea ethers, acylpseudothiourea ethers and diacylpseudothiourea ethers, can be prepared by combining isocyanates, mustard oils, and acyl rhodanides with imido esters. The imido esters immediately combine with phenyl isocyanate, at ordinary temperatures, giving a quantitative yield of an addition product as follows:



$$C_6H_5C\langle\begin{matrix}NH\\OR\end{matrix} + CONC_6H_5 = C_6H_5C\langle\begin{matrix}NCONHC_6H_5\\OR\end{matrix}$$

This class of compounds, perhaps, may be called ureaimido esters or carbamidimido esters, since they have the structure of imido esters and ureas combined. They are extremely sensitive towards hydrogen chloride by which reagent, just as the acylpseudourea ethers[1] (II) they are readily and quantitatively converted in the cold, with loss of alkyl chloride, into acylureas.

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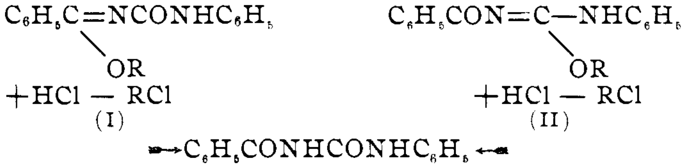
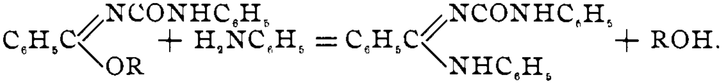
[1] Stieglitz and Dains: This Journal, **21**, 136.

This reaction with these two classes of compounds proceeds as follows:



$$\mathrm{C_6H_5C(OR){=}NCONHC_6H_5 + HCl - RCl}\ \text{(I)} \longrightarrow \mathrm{C_6H_5CONHCONHC_6H_5} \longleftarrow \mathrm{C_6H_5CON{=}C(OR){-}NHC_6H_5 + HCl - RCl}\ \text{(II)}$$

It will be noticed that the imido ester grouping in the different positions in these isomers are affected alike, inasmuch as under similar conditions both compounds give with hydrogen chloride the same derivative, benzoylphenylurea. The ureaimido esters (I) readily react with aniline, at the temperature of the steam-bath, and ureaamidines are formed as follows:

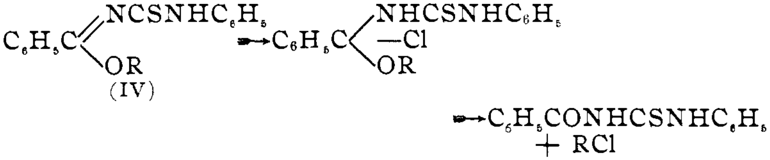


$$\mathrm{C_6H_5C}\left\langle\begin{array}{l}\mathrm{NCONHC_6H_5}\\ \mathrm{OR}\end{array}\right. + \mathrm{H_2NC_6H_5} = \mathrm{C_6H_5C}\left\langle\begin{array}{l}\mathrm{NCONHC_6H_5}\\ \mathrm{NHC_6H_5}\end{array}\right. + \mathrm{ROH.}$$

(III)

Whether the structure shown in formula (III) or the tautomeric form is to be assigned to these amidines must be decided later. These amidines have little or no basic properties.

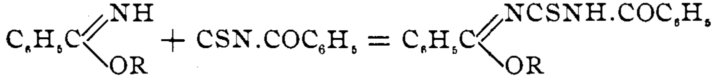
The mustard oils, phenylmustard oil and allyl mustard oil, react less energetically than phenyl isocyanate with the imido esters. On long standing or on warming, the mixtures deposit crystals. These compounds, for which the name thioureaimido esters (IV) is proposed, are closely similar to the above oxygen analogues, since with hydrogen chloride, under similar conditions, they readily separate alkyl chloride and give the corresponding acylthio ureas. The mechanism of the reaction is as follows:



$$\mathrm{C_6H_5C}\left\langle\begin{array}{l}\mathrm{NCSNHC_6H_5}\\ \mathrm{OR}\end{array}\right. \text{(IV)} \longrightarrow \mathrm{C_6H_5C}\left\langle\begin{array}{l}\mathrm{NHCSNHC_6H_5}\\ \mathrm{-Cl}\\ \mathrm{OR}\end{array}\right. \longrightarrow \mathrm{C_6H_5CONHCSNHC_6H_5 + RCl}$$

The isomeric acylpseudothiourea ethers and the diacylpseudothiourea ethers apparently have not yet been prepared, so that a comparison of the behavior of these compounds with the thioureaimido ester derivatives must be deferred to a later date.

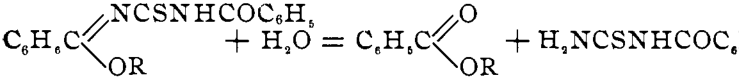
When the thioureaimido esters are warmed with aniline, and other organic bases, thioureaimidines are formed. Like the above ureaamidines they appear to have no basic properties. The fact that they are not soluble in alkali affords new evidence that the double union of the imido ester grouping confers a basic nature to the molecules. Here, however, it is neutralized by the negative character of the urea group. The imido esters combine with acetyl and benzoyl thiocyanates with evolution of heat, the mixtures readily solidifying. Acylthioureaimido esters (V) are then produced, as follows:



$$C_6H_5C\left<\begin{matrix}NH\\ OR\end{matrix}\right. + CSN.COC_6H_5 = C_6H_5C\left<\begin{matrix}NCSNH.COC_6H_5\\ OR\end{matrix}\right.$$

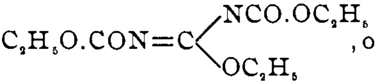
(V)

These compounds are formed more readily than the above and they are far more unstable than the thioureaimido esters. When they are warmed with hydrochloric acid they decompose in a different manner from the other types of ureaimido esters. A monoacylthiourea, and not a diacyl derivative, is obtained. The decomposition under this treatment takes place at the double union as follows:



$$C_6H_6C\left<\begin{matrix}NCSNHCOC_6H_5\\ OR\end{matrix}\right. + H_2O = C_6H_5C\left<\begin{matrix}O\\ OR\end{matrix}\right. + H_2NCSNHCOC_6H_5$$

(VI)

What appears to be the nearest known analogue to a metamer of the above or dibenzoylpseudothiourea ether is the ethylisodicarbethoxyurea,  $C_2H_5O.CON{=}C\left<\begin{matrix}NCO.OC_2H_5\\ OC_2H_5\end{matrix}\right.$, of Dains.[1] This compound is also very sensitive towards hydrogen chloride; however, it does not separate at the double union, like the above, but decomposes with the evolution of ethyl chloride, giving the diacylurea, $C_2H_5OCONHCONHCO.OC_2H_5$. The ease with which the ureaimido esters decompose with hydrochloric acid, without forming a stable intermediate addition product or "salt," recalls the perfectly analogous behavior of the acylimido esters.[2] In the case of the latter, the above two reactions with

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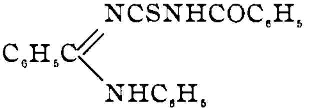
[1] *Loc. cit.*

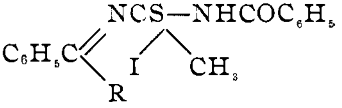
[2] Wheeler, Walden and Metcalf: *Am. Chem. J.*, 19, 129 and 20, 64.

hydrogen chloride were also observed. The properties of the ureaimido esters, in general, approach more nearly to those of the acylimidoesters than to those of other types of imido esters.

When the acylthioureaimido esters are treated with aniline, toluidine, etc., acylthioureaamidines (VII) are formed in the normal manner. These compounds, as well as the thioureaimido esters, combine with alkyl halides, the addition probably taking place to the sulphur as shown in formula (VIII).



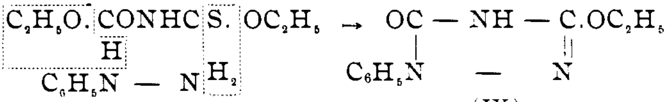
(VII)



(VIII)

The action of phenylhydrazine on the acylthioureaimido esters seemed theoretically promising for the preparation of triazole derivatives; but it appears, from preliminary experiments, that, although hydrogen sulphide is evolved in this treatment, triazoles do not result, at least not as the chief product. The hydrogen sulphide, first formed, decomposes a part of the ureaimido ester, giving benzoylthiourea, etc.

Experiments in this laboratory by Dr. Bayard Barnes have shown that the acylphenylthioureas react with aniline and phenylhydrazine with the removal of the acyl group. With phenylhydrazine no triazole derivative was obtained. Similar results were obtained with the acylphenylurethanes, acetylphenylurethane, formylphenylurethane[1] and acetylphenylthiourethane. It is probable that other diacylanilides will be found to act similarly. On the other hand those acylurethanes which do not contain a phenyl group such as acetylurethane,[2] acetyl- and benzoylthionurethane, give triazole derivatives. Dr. Barnes has also found that carbethoxythionurethane of Delitsch[3] readily reacts with phenylhydrazine as follows:



$$\begin{array}{l} C_2H_5O.CONHCS.OC_2H_5 \\ \quad\; H \\ \;\; C_6H_5N - NH_2 \end{array} \rightarrow \begin{array}{ccccc} OC & - & NH & - & C.OC_2H_5 \\ | & & & & \| \\ C_6H_5N & & - & & N \end{array}$$

(IX)

That the compound formed in this reaction is 1-phenyl-3-

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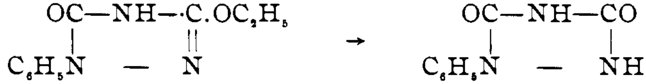
[1] Wheeler and Metcalf: *Am. Chem. J.*, **19**, 217.

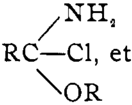
[2] Andreocci: *Ber. d. chem. Ges.*, **22**, R. 737; *Ibid.*, **24**, R., 203.

[3] *J. prakt. Chem.*, **10**, 118.

ethoxy-5-triazolon, and that it has the structure represented by formula (IX), is shown by its behavior, on boiling with strong hydrochloric acid, whereupon it is converted into Pinner's[1] urazole, (X):



(X)

The process which in general serves for the preparation of simple or monosubstituted ureas and thioureas, and which consists of treating a salt of an amine with potassium cyanate or thiocyanate, does not lead to the formation of the prototypes of the above urea derivatives, when applied to the salts of the imido esters. This fact seems to the writer to be a strong argument in support of the theory of Stieglitz that the salts of the imido esters are not ammonium derivatives, but that they are derived from the form  $RC(NH_2)(Cl)(OR)$, etc. In fact, the properties of the cyanic and thiocyanic acid salts do not agree with those which would be expected for salts having an ammonium structure.

When ice-cold solutions of benzimidoisobutyl ester hydrochloride and potassium cyanate, in molecular proportions, are mixed together, a mass of well-crystallized, colorless prisms separate. If an attempt is made to filter these at ordinary temperature they rapidly decompose, giving off a gas (CO_2?), and completely liquefying. Owing to the unstable nature of this salt, which is undoubtedly a cyanate, it was not examined further. On the other hand, the corresponding thiocyanic salt is far more stable. It can be prepared, at ordinary temperature, by mixing solutions of the imido ester hydrochloride with potassium thiocyanate, whereupon a bulky mass of colorless prisms or needles separate. This salt has the structure represented by formula (XI), and all attempts to rearrange it into the metameric thioureaimido ester (XII) failed.

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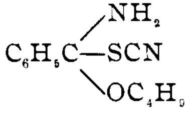
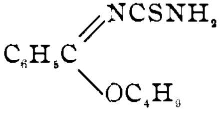
[1] *Ber. d. chem. Ges.*, **21**, 1219.



$$C_6H_5C\begin{array}{l}\diagup NH_2\\ -SCN\\ \diagdown OC_4H_9\end{array}$$

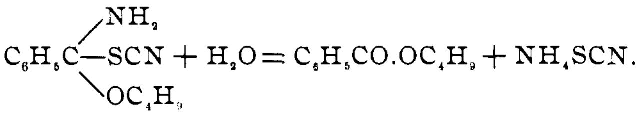
(XI)



$$C_6H_5C\begin{array}{l}\diagup\!\!\diagup NCSNH_2\\ \diagdown OC_4H_9\end{array}$$

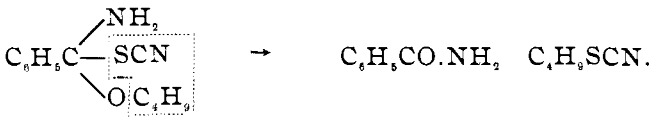
(XII)

When this salt is warmed in aqueous solution it dissolves, but the solution almost immediately becomes turbid and an oil (isobutyl benzoate) separates. On evaporating to dryness nothing but ammonium thiocyanate is obtained. The decomposition then proceeds as follows :



$$C_6H_5C\begin{array}{l}\diagup NH_2\\ -SCN\\ \diagdown OC_4H_9\end{array} + H_2O = C_6H_5CO.OC_4H_9 + NH_4SCN.$$

If the dry salt is heated above its melting-point it decomposes smoothly as follows :

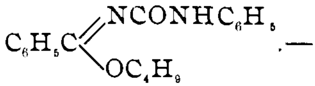


$$C_6H_5C\begin{array}{l}\diagup NH_2\\ -SCN\\ \diagdown OC_4H_9\end{array} \rightarrow \quad C_6H_5CO.NH_2 \quad C_4H_9SCN.$$

It will be noticed that these reactions are analogous in every respect to those of the hydrochloric acid salts of the imido esters.

EXPERIMENTAL PART.

Phenylureaimidoisobutyl Benzoate,



$$C_6H_5C\begin{array}{l}\diagup\!\!\diagup NCONHC_6H_5\\ \diagdown OC_4H_9\end{array}.—$$

Phenyl isocyanate (3.4 grams) and benzimidoisobutyl ester (10 grams) combined with evolution of heat and the mixture solidified to a white mass. When this was crystallized from alcohol, colorless prisms were obtained which melted from 99°–100°. A nitrogen determination gave :

	Calculated for $C_{18}H_{20}N_2O_2$.	Found.
Nitrogen	9.4	9.1

Action with Hydrogen Chloride.—Some of the above material was dissolved in benzene and the solution was saturated with hydrogen chloride whereupon colorless prisms separated, melting at about 200°. This material proved to be *Benzoylphenylurea*, $C_6H_5CONHCONHC_6H_5$, which crystallized from alcohol in long silky needles, and on boiling it with sodium hydroxide it gave phenylurea.

The extreme sensitiveness of compounds of this type towards hydrochloric acid was shown by the fact that it was found to be impossible to isolate ureaimido esters from benzimidomethyl, ethyl, and phenylacetimidomethyl esters and phenyl isocyanate, if the latter contained phosphorus oxychloride. Under these conditions the benzimido esters gave *benzoylphenylurea*, while phenylacetimidomethyl ester gave a compound very difficultly soluble in alcohol. It crystallized in the form of needles and melted at 166° and a nitrogen determination showed that it was *phenylacetylphenylurea*, $C_6H_5CH_2CONHCONHC_6H_5$:

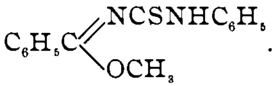
	Calculated for $C_{15}H_{14}N_2O_2$.	Found.
Nitrogen	11.0	11.0

Action with Aniline.—Phenylureaimidoisobutyl benzoate (2 grams) and aniline (0.6 gram), were mixed in benzene and warmed on the water-bath whereupon a substance separated in granular crystals. It was found to be very difficultly soluble in alcohol (a property of ureaamidines, which is general as far as we have observed, and on boiling with alcohol it melted from 179°-180°. A nitrogen determination agreed with the figures calculated for *benzenylphenylureaphenylamidine*, $C_6H_5NH—(C_6H_5)C = NCONHC_6H_5$.

	Calculated for $C_{20}H_{17}N_3O$.	Found.
Nitrogen	13.3	13.0

This amidine is insoluble in dilute hydrochloric acid and no hydrochloric acid salt was obtained when the material was dissolved in benzene and saturated with hydrogen chloride. It is insoluble in alkali.

Phenylthioureaimidomethyl Benzoate,



$$C_6H_5C\begin{matrix}\diagup\!\!\diagup NCSNHC_6H_5\\ \diagdown OCH_3\end{matrix}$$

.—Equal quantities of benzimidomethyl ester and phenyl mustard oil (5 grams of each) were mixed and kept at a temperature of about 60°-70° for two days. On cooling, then, the mixture solidified almost completely. In each of the experiments with phenyl mustard oil and the imido esters, a yellow mixture resulted although the ingredients before mixing were colorless.

On crystallizing from alcohol beautiful colorless or cream-colored lozenge-shaped tables were obtained which melted sharply at 132°. The material is readily soluble in benzene and hot alcohol, difficultly in cold alcohol, and a nitrogen determination gave:

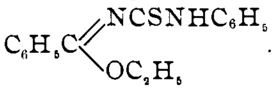
	Calculated for $C_{15}H_{14}N_2OS$.	Found.
Nitrogen	10.37	10.29

When this compound was treated with cold dilute hydrochloric acid, in which it is insoluble, little or no action was observed after two days' standing. When a little alcohol was added and the whole was warmed, effervescence took place, methyl chloride was evolved, and, on cooling, the long characteristic colorless needles of *benzoylphenylthiourea*, $C_6H_5CONH-CSNHC_6H_5$, were obtained, melting about 148°.

Benzenylphenylthiourea-p-anisylamidine,

$C_6H_5C\begin{cases}NCSNHC_6H_5\\NHC_6H_4OCH_3\end{cases}$.—Molecular quantities of the above imido ester and *p*-anisidine were mixed in benzene solution and allowed to stand at a temperature of about 70° for several hours, whereupon a mass of plates or scales separated. This material was very difficultly soluble in alcohol and in benzene. When crystallized from these solvents and from amyl acetate, it melted at about 180°. A satisfactory nitrogen determination was not obtained, undoubtedly owing to the fact that this substance, as well as the corresponding phenyl and naphthyl amidines, burn with great difficulty, the results invariably coming low.

Phenylthioureaimidoethyl Benzoate,

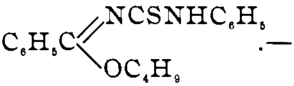


$C_6H_5C\begin{cases}NCSNHC_6H_5\\OC_2H_5\end{cases}$.—

Benzimidoethylester (5 grams) and phenyl mustard oil (4.5 grams) gave a yellow oil directly on mixing. After two days the material solidified to a glistening mass of flattened prisms or tables and on crystallizing from alcohol it separated in the form of cream-colored tables and it melted sharply at 119°. These thioureaimido esters, in general, show a great tendency to crystallize. A nitrogen determination gave:

	Calculated for $C_{16}H_{16}N_2OS$.	Found.
Nitrogen	9.8	9.7

When treated with hydrochloric acid it behaved precisely like the methyl ester and benzoylphenylthiourea was obtained.

Phenylthioureaisobutyl Benzoate,  $C_6H_5C\begin{array}{l}\diagup\!\!\diagup NCSNHC_6H_5\\ \diagdown OC_4H_9\end{array}$.—Benzimidoisobutyl ester (5 grams) and phenyl mustard oil (3.8 grams) behaved, on mixing and standing, precisely like the above. When crystallized from alcohol it forms large, stout tables and it melts at 125°. A nitrogen determination gave:

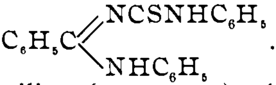
	Calculated for $C_{18}H_{20}N_2OS$.	Found.
Nitrogen	8.9	8.9

When this was treated with hydrochloric acid and warmed, *benzoylphenylthiourea* was obtained.

When 2 grams of this imido ester were warmed on the water-bath with aqueous-alcoholic ammonia for a number of hours and then allowed to cool, colorless crystals separated melting from 151°–153°. A nitrogen determination gave 18.5 per cent., while the calculated for benzenylphenylthiourea amidine is 27.0 per cent., and that for phenylthiourea which melts at 154° is 18.4 per cent. The material, in fact, had the bitter taste and other properties of *phenylthiourea*.

When this thioureaimido ester was treated with methyl iodide a varnish was obtained which crystallized after long standing.

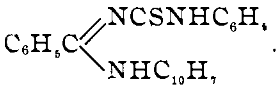
Phenylthioureaisobutyl benzoate readily reacts with phenyl hydrazine, giving off hydrogen sulphide and it gives a compound which crystallizes in plates when treated with benzoyl chloride. These reactions will receive more thorough attention later.

Benzenylphenylthioureaphenylamidine,  $C_6H_5C\begin{array}{l}\diagup\!\!\diagup NCSNHC_6H_5\\ \diagdown NHC_6H_5\end{array}$.—The above imido ester (4 grams) and aniline (1.1 grams) after warming on the water-bath gave off only a trace of hydrogen sulphide. The product, on crystallizing from alcohol, formed a beautiful mass of large thin plates. They melted from 151°–152° and a nitrogen determination gave:

	Calculated for $C_{20}H_{17}N_3S$.	Found.
Nitrogen	12.6	12.0

This material is insoluble in cold hydrochloric acid, concentrated or dilute. On warming, it dissolves, but on cooling it crystallizes out again unaltered. Platinum chloride precipitates a curdy yellow mass from the concentrated hydrochloric acid solution.

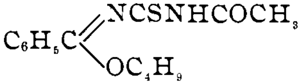
Benzenylphenylthiourea-β-naphthylamidine,



$C_6H_5C\begin{cases}NCSNHC_6H_5\\NHC_{10}H_7\end{cases}$

.—The above imido ester readily reacts with β-naphthylamine, giving a compound that crystallizes in minute plates and which is extremely insoluble in the ordinary organic solvents; when crystallized from alcohol and amyl acetate it melted, not sharply, from 182°–183°. The material burned very slowly and a satisfactory nitrogen determination was not obtained, the calulated being 11.0 per cent. while 10.0 was found.

Acetylthioureaimidoisobutyl Benzoate,



$C_6H_5C\begin{cases}NCSNHCOCH_3\\OC_4H_9\end{cases}$

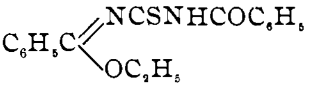
—Benzimidoisobutyl ester and acetyl thiocyanate combine with evolution of considerable heat and, on cooling, the mixture completely solidifies, whereupon, on crystallizing from alcohol, colorless needles are obtained which melt from 125°–126°. A nitrogen determination gave:

	Calculated for $C_{14}H_{18}N_2O_2S$.	Found
Nitrogen	10.0	9.9

When this imido ester was treated in alcoholic solution with hydrogen chloride a compound was obtained melting at 166° and which had all the properties of *acetylthiourea*, $CH_3CONHCSNH_2$.

With phenylhydrazine it evolves hydrogen sulphide, and on crystallizing the product from alcohol acetylthiourea separates.

Benzoylthioureaimidoethyl Benzoate,



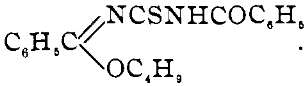
$C_6H_5C\begin{cases}NCSNHCOC_6H_5\\OC_2H_5\end{cases}$

—When benzimidoethyl ester (6.1 grams) was mixed with 5.6 grams of benzoyl sulphocyanate the mixture completely solidified. On crystallizing from alcohol, needles were obtained which melted from 131°–132°, and on analysis the following result was obtained:

	Calculated for $C_{17}H_{16}N_2O_2S$.	Found.
Nitrogen	8.9	8.8

When this imido ester was warmed with phenylhydrazine the only crystalline material obtained was *benzoylthiourea*.

Benzoylthioureaimidoisobutyl Benzoate,



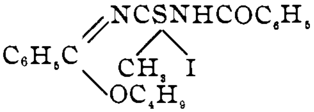
$C_6H_5C\begin{matrix} /\!\!/ NCSNHCOC_6H_5 \\ \diagdown OC_4H_9 \end{matrix}$.

—When benzimidoisobutyl ester (10 grams) and benzoyl sulphocyanate (7.4 grams) were mixed, considerable heat was evolved and the mass solidified. When this was crystallized from alcohol, colorless needles, melting at 120,° were obtained. A nitrogen determination gave:

	Calculated for $C_{19}H_{20}N_2O_2S$.	Found.
Nitrogen	8.2	8.4

When this imido ester was treated with hydrogen chloride in benzene solution, *benzoylthiourea*, melting at 169°–170° was obtained. Apparently this same compound was obtained when the ester was treated with ammonia, phenylhydrazine and with benzoyl chloride. These results show the great tendency this ester has to separate at the double bond.

Benzoylthioureaimidoisobutyl Benzoate Methyl Iodide,



$C_6H_5C\begin{matrix} /\!\!/ NCSNHCOC_6H_5 \\ CH_3\ \ I \\ \diagdown OC_4H_9 \end{matrix}$

—The above imido ester and methyl iodide combine in benzene solution to form a compound containing iodine and which crystallizes from alcohol in well-developed, colorless prisms melting from 204°–205.° A nitrogen determination gave:

	Calculated for $C_{20}H_{23}N_2O_2SI$.	Found.
Nitrogen	5.7	5.7

Benzenylbenzoylthioureaphenylamidine,

$C_6H_5C\begin{matrix} /\!\!/ NCSNHCOC_6H_5 \\ \diagdown NHC_6H_5 \end{matrix}$.

—When molecular proportions of the above imido ester and aniline were heated in benzene solution a substance was obtained which crystallized in colorless prisms and which melted from 145°–146°. A nitrogen determination gave:

	Calculated for $C_{21}H_{17}N_3OS$.	Found.
Nitrogen	11.6	11.2

No hydrochloric acid salt was obtained when this amidine was treated with hydrogen chloride.

Benzenylbenzoylthioureaorthotolylamidine,

$$C_6H_5C\left\langle\begin{matrix}NCSNHCOC_6H_5\\ NHC_6H_4CH_3\end{matrix}\right.$$

.—This compound was obtained on fusing the imido ester with ortho toluidine. It crystallized from alcohol in colorless prisms which melted from 116°–117° and a nitrogen determination gave:

	Calculated for $C_{22}H_{19}N_3OS$	Found.
Nitrogen..................	11.2	10.8

Benzoylthioureaimidomethylphenyl Acetate,

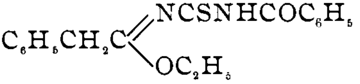
$$C_6H_5CH_2C\left\langle\begin{matrix}NCSNHCOC_6H_5\\ OCH_3\end{matrix}\right.$$

.—When phenylacetimidomethyl ester (5.6 grams) was treated with benzoylthiocyanate (5 grams), the mixture solidified immediately. It was crystallized from alcohol and obtained in the form of colorless needles melting from 116°–117°. A nitrogen determination gave:

	Calculated for $C_{17}H_{16}N_2O_2S$.	Found.
Nitrogen	8.9	9.3

When this imido ester was treated with phenylhydrazine, hydrogen sulphide was evolved but the product, on crystallizing from alcohol, was neither an amidine or a triazole. It contained 15.4 per cent. of nitrogen while the calculated for *benzoylthiourea* is 15.5 per cent. It agreed in all its properties with the acylthiourea.

Benzoylthioureaimidoethylphenyl Acetate,

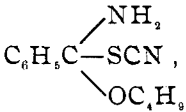


$$C_6H_5CH_2C\left\langle\begin{matrix}NCSNHCOC_6H_5\\ OC_2H_5\end{matrix}\right.$$

, was prepared from phenylacetimidoethyl ester. It forms colorless needles from alcohol which melt from 140°–141°. When treated with hydrogen chloride in alcoholic solution it gave small prismatic crystals, melting from 169°–170°, and a nitrogen determination agreed with the calculated for benzoylthiourea:

	Calculated for $C_8H_8N_2SO$.	Found.
Nitrogen	15.5	15.6

The Thiocyanic Acid Salt of Benzimidoisobutyl Ester,


$C_6H_5C\begin{cases}NH_2\\ SCN\\ OC_4H_9\end{cases}$

, is readily formed on mixing aqueous solutions of the imido ester hydrochloride and potassium cyanate. It then separates as a mass of colorless needles or prisms which are quite difficultly soluble in water. It melts at about 130°. A portion dried in a desiccator over calcium chloride and then for a few minutes at 60°–70° gave the following results on analysis:

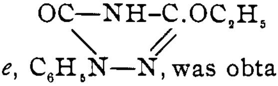
	Calculated for $C_{12}H_{16}N_2SO$.	Found.
Nitrogen	11.8	11.9

Its reaction with iron chloride and with alkali showed that this material was a salt of the imido ester and not the isomeric thioureaimidoisobutyl benzoate. It decomposes on warming with water smoothly into ammonium thiocyanate and isobutyl benzoate and when heated above its melting-point it gives benzamide and isobutyl thiocyanate.

EXPERIMENTS BY BAYARD BARNES.

Carbethoxythioncarbamic Ester, $C_2H_5OCONHCS.OC_2H_5$.—This was prepared according to the directions of Delitsch;[1] when purified by means of its potassium salt, it was found to boil unaltered at 135° at 13 mm. pressure. It melts at 44°.

1-Phenyl-3-ethoxy-5-triazolone,


$\begin{array}{c}OC—NH—C.OC_2H_5\\ \diagdown\quad\diagup\\ C_6H_5N—N\end{array}$

, was obtained when the above carbamic ester (15 grams) was heated with phenylhydrazine (9 grams) on the steam-bath. After the evolution of hydrogen sulphide and alcohol had ceased, the material was crystallized from hot water, whereupon colorless needles, melting from 150°–151°, were obtained. This material was soluble in alkali and was precipitated unaltered by acids. It contained no sulphur and on analysis the following results were obtained:

	Calculated for $C_{10}H_{11}N_3O_2$.	Found.
Carbon	58.5	58.9
Hydrogen	5.2	5.3
Nitrogen	20.5	20.4

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[1] *J. prakt. Chem.*, 10, 118.

When this compound was boiled for some time with concentrated hydrochloric acid and alcohol, colorless plates were obtained, which melted at 263°, showing signs of melting at 255°. For purposes of comparison Pinner's[1] urazole was prepared and it was found to be identical with the above.

Acetylphenylurethane, $CH_3CO(C_6H_5)NCO.OC_2H_5$.—Ten grams of phenylurethane were boiled with an equal weight of acetic anhydride for several hours whereupon, on pouring into water, unaltered urethane was obtained. Acetyl chloride was then added and boiled for about one hour. Then about one-half of the solution was distilled off at ordinary pressure and the remainder at 10 mm. pressure whereupon the material practically all boiled from 142°–143°. It was thus obtained as a colorless oil which, like formylphenylurethane, refused to solidify on cooling. A nitrogen determination gave :

	Calculated for $C_{11}H_{13}NO_3$.	Found.
Nitrogen	6.7	7·3

When this compound was gently warmed with phenylhydrazine and the product was crystallized from benzene, colorless plates, melting at 128°, were obtained. The following nitrogen determination showed that this material was not a triazole derivative but rather *acetylphenylhydrazine* :

	Calculated for $C_8H_{10}N_2O$.	Found.
Nitrogen	18.6	18.0

The action of phenylhydrazine on Hugershoff's[2] *acetylphenylthiocarbamide*, $CH_3CONHCSNHC_6H_5$, melting at 139°, although some hydrogen sulphide was evolved, did not lead to the formation of a triazole derivative, at least not as the chief product. The material that separated, on crystallizing from alcohol, formed large, four-sided plates melting at 153° and having all the properties of *phenylthiourea*. In other words the action of phenylhydrazine, in this case, removes the acetyl group.

NEW HAVEN, CONN., May 29, 1900.

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[1] *Loc. cit.*

[2] *Ber. d. chem. Ges.*, **32**, 3658.