cent. of the break. This, figured to P_2O_5, amounted to 57 per cent. of the ash in the break. It would seem unjustifiable to calculate the phosphorus present in the linseed oil to lecithin, on account of the large percentage of bases present. Inasmuch as albuminoids coagulate at a low temperature as compared with the breaking temperature of linseed oil, we feel that any assumption that albuminoids are present is unjustified. We do, however, feel justified in saying that the principal cause of the break in linseed oil is the phosphates of lime and magnesia present, although their presence in the oil may be due to a combination between them and some organic base or bases.

[CONTRIBUTIONS FROM THE SHEFFIELD LABORATORY OF YALE UNIVERSITY.]

ON A CLASS OF PSEUDOTHIOUREAS DESCRIBED AS NORMAL UREAS.

BY HENRY L. WHEELER AND GEORGE S. JAMIESON.

Received April 22, 1903.

WHEN thioamides are treated with alkyl halides, compounds are formed having the alkyl group attached to sulphur. In the normal thioureas, for example, it is the sulphur and not the nitrogen that is the point of attack. When a radical is attached to sulphur then further alkylation may take place on the nitrogen.[1] At least this has been found to be true in all cases that have been thoroughly examined.

There are some thioureas, however, that have been represented as yielding nitrogen alkyl derivatives with halides. Wunderlich[2] found that sodium cyanamide unites with mustard oils in alcoholic solution, giving the sodium salts of alkylcyanthioureas RNHCSNHCN, and by treating these salts with alkyl halides the sodium was shown to be replaced by alkyls. The resulting dialkyl compounds were represented by the general formula RNH—CSNR'CN.

Later, Hecht[3] prepared a large number of these compounds. He represents them by the formula above, but he remarks that further work will be necessary to determine their structure and he states that this will be the subject of a later paper. Thirteen years

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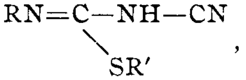
[1] Bertram : *Ber. d. chem. Ges.*, **25**, 48 (1892).

[2] *Ber. d. chem. Ges.*, **19**, 448 (1886).

[3] *Ber. d. chem. Ges.*, **23**, 1658 (1890).

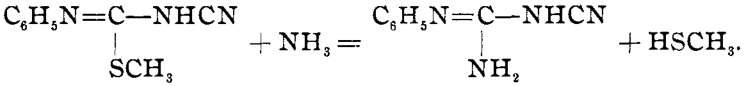
have now passed and these compounds have not been further examined. From what has just been said, it seemed doubtful that the entering alkyl group attaches itself to nitrogen. We therefore undertook the determination of the structure of these ureas, and we will now show that they are incorrectly represented in the literature—that they are pseudothioureas and not derivatives of normal thioureas. Their structure is to be represented by the general formula



$$RN{=}\underset{\substack{\diagdown\\ SR'}}{C}{-}NH{-}CN,$$

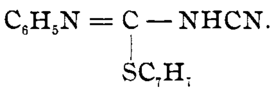
in which R′ is the alkyl of the alkyl halide.

Sodium cyanamide was treated in alcoholic solution with phenyl mustard oil. The crystalline salt thus obtained was heated with methyl iodide according to the directions of Hecht. The pure product melted, as he states, at 186°. When this was suspended in strong alcoholic ammonia, a reaction slowly took place and methyl mercaptan made its presence known. In order to get a complete reaction, it was necessary to heat in a closed tube at 90°-95°. The crystalline product was then free from sulphur and, on analysis, gave results agreeing with those calculated for phenylcyanguanidine. The reaction took place as follows:



$$C_6H_5N{=}\underset{\substack{|\\ SCH_3}}{C}{-}NHCN + NH_3 = C_6H_5N{=}\underset{\substack{|\\ NH_2}}{C}{-}NHCN + HSCH_3.$$

In addition to the above phenylcyanthiolmethylpseudothiourea, we have prepared and examined phenylcyanthiolbenzylpseudothiourea, the phenylthiocarbaminbenzylcyamide of Hecht. This compound has the structure



$$C_6H_5N = \underset{\substack{|\\ SC_7H_7}}{C} - NHCN.$$

We find also that it is identical with Fromm's phenyl-ψ-benzylsulphoharnstoffcyanide, a fact which apparently escaped the notice of Professor Fromm.[1] He gives the melting-point at 190°. Hecht states that the substance melts at 182°. We have prepared the compound by both methods and both preparations melted at 182°-183°. When mixed, the melting-point was not altered. We have also prepared the corresponding methyl deriva-

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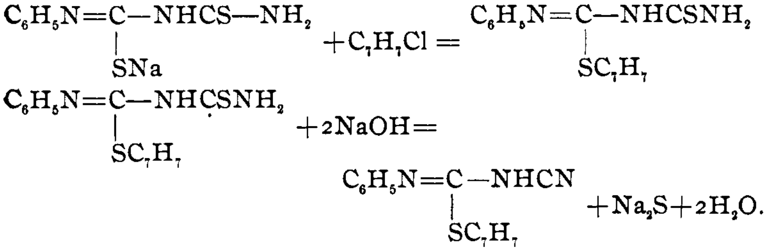
[1] *Ber. d. chem. Ges.*, **28**, 1304 (1895).

tive by both methods and find that these products are identical.

The preparation of Hecht's compounds by Fromm's method offers further proof that the compounds are pseudothioureas. This method consists in treating phenyldithiobiuret with three molecular proportions of alkyl halide and four of alkali. The reaction is represented as follows:



$$C_6H_5N{=}\underset{\substack{|\\ SNa}}{C}{-}NHCS{-}NH_2 + C_7H_7Cl = C_6H_5N{=}\underset{\substack{|\\ SC_7H_7}}{C}{-}NHCSNH_2$$

$$C_6H_5N{=}\underset{\substack{|\\ SC_7H_7}}{C}{-}NHCSNH_2 + 2NaOH = C_6H_5N{=}\underset{\substack{|\\ SC_7H_7}}{C}{-}NHCN + Na_2S + 2H_2O.$$

Fromm has shown that when the phenylcyanthiolbenzylpseudothiourea is boiled with hydrochloric acid it takes up the elements of water and separates aniline, forming thiolbenzylallophanic ester, $C_7H_7S.OC{-}NHCONH_2$. This shows that the alkyl group is attached to sulphur.

The pseudothioureas containing a —CN group are more stable and less reactive than other pseudothioureas. They have acid properties and form salts even with ammonia.

It was found that phenylcyanthiolbenzylpseudothiourea could be crystallized unaltered from boiling acetic anhydride. Benzoyl chloride failed to react with the compound in the Schotten-Baumann process, and little or no mercaptan was given off on heating on the steam-bath or at 150° with aniline or with phenylhydrazine. These compounds, therefore, depart widely in properties from other classes of pseudothioureas.

Phenylcyanguanidine, $C_6H_5N{=}C({-}NH_2){-}NHCN$.—Phenylcyanthiolmethylpseudothiourea was heated with an excess of alcoholic ammonia at 90°-95° for five hours. Mercaptan escaped, on opening the tube, and from the alcoholic solution bunches of colorless needles were obtained. These were moderately soluble in warm alcohol and could be crystallized from water. The substance dissolved in warm alkali and was precipitated by mineral acids. It melted at 190°-191° without decomposition, and a nitrogen determination gave:

	Calculated for $C_8H_8N_4$.	Found.
Nitrogen	35.0	35.2

The *ammonium salt* of phenylcyanthiolmethylpseudothiourea was obtained when the pseudothiourea was heated at 100° for five hours with alcoholic ammonia saturated with hydrogen sulphide. On cooling, no pressure was found in the tube and, on concentrating the solution, colorless needles separated which, after two recrystallizations, melted at about 142°-143° to a pale yellow liquid. A nitrogen determination gave:

	Calculated for $C_6H_5N=C(—SCH_3)—NHCN.NH_3C_9H_{12}N_4S$.	Found.
Nitrogen....................	26.82	26.79

NEW HAVEN, CONN., April 17, 1903.

THE BASIC OXALATES OF BISMUTH.

BY F. B. ALLAN.

Received May 20, 1903.

IN recent papers the author has given the results of researches on the nitrates[1] and sulphates[2] of bismuth, making use of the phase rule to determine the number of phases present, and thus to know whether the solid to be analyzed was one phase or a mixture of two phases. In a monovariant system of three components, we may have a gaseous, a liquid, and two solid phases. In a divariant system, only three phases can exist and there can be only one solid in addition to the liquid and gaseous phases, and it is only in the latter case that we can call the solid a chemical compound. In the experiments referred to, both monovariant and divariant systems were obtained, but as three weeks were sometimes necessary to obtain equilibrium in a monovariant system, no attempt has been made to get other than divariant systems in this research.

Heintz[3] added oxalic acid to a solution of bismuth oxide in nitric acid, and boiled the precipitate repeatedly with water. He supposed that the neutral oxalate is first formed, and that it is decomposed by water; he gives the resulting substance the formula $Bi_2O_32C_2O_31\frac{1}{2}H_2O$. Schwartzenberg[4] boiled bismuth oxide with acid potassium oxalate, and the product dried at 100° agreed with the formula $Bi_2O_33C_2O_34H_2O$. Souchay and Lensson[5] prepared the neutral oxalate and gave the composition of the air-dried salt

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[1] *Am. Chem. J.*, **25**, 307.

[2] *Ibid.*, **27**, 284.

[3] Pogg. *Ann.*, **63**, 90.

[4] *Ann. Chem.* (Liebig), **64**, 127.

[5] *Ibid.*, **105**, 245.