p-Propionaminobenzonitrile.—This was prepared by heating the aminonitrile for several hours with propionic anhydride, and crystallizing the crude product from water. It forms crystals melting at 169°. Percentage of nitrogen found by analysis, 16.09; calculated for $C_2H_5CONHC_6H_4CN$, 16.06.

p-Aminobenzamide.—The aminonitrile was warmed for some time at 50° with alkaline hydrogen dioxide solution. On cooling, white crystals separated, melting-point 178°-179°. Not sufficient of the material was prepared for further purification, so that the melting-point as given is probably low. Reichenbach and Beilstein[1] report the melting-point of *p*-aminobenzamide as 178°-179°, but Remsen and Reed[2] give the corrected melting-point as 182.9°.

p-Aminobenzthiamide, $H_2NCSC_6H_4CN$.—The aminonitrile was dissolved in alcohol, the solution saturated at 0° with dry ammonia and dry hydrogen sulphide, and then heated in a sealed tube at 100° for several hours. The crystals obtained, when purified and dried, showed a melting-point of 172°. Engler[3] gives the melting-point of *p*-aminobenzthiamide as 170°.

The study of *p*-aminobenzonitrile and of its derivatives is being continued.

ORGANIC LABORATORY, HAVEMEYER HALL, COLUMBIA UNIVERSITY, March, 1903.

[CONTRIBUTIONS FROM THE SHEFFIELD LABORATORY OF YALE UNIVERSITY.]

ON THE MOLECULAR REARRANGEMENT OF THIOCYANACETANILIDES INTO LABILE PSEUDOTHIOHYDANTOINS; AND ON THE MOLECULAR REARRANGEMENT OF THE LATTER INTO STABLE ISOMERS.

BY TREAT BALDWIN JOHNSON.

Received March 1, 1903.

[SECOND PAPER.]

IN a previous paper from this laboratory by Wheeler and Johnson,[4] it was shown that a thiocyanacetanilide is capable of a

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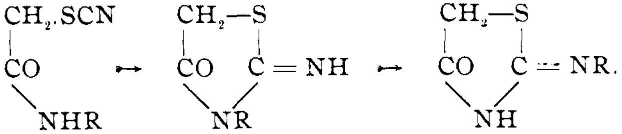
[1] *Ann. Chem.* (Liebig), **132**, 137 (1864).

[2] *Am. Chem. J.*, **21**, 281 (1899).

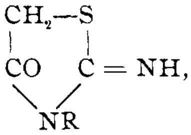
[3] *Ztschr. phys. Chem.*, 1868, p. 613; *Ann. Chem.* (Liebig), **149**, 297 (1869).

[4] *Am. Chem. J.*, **28**, 121 (1902).

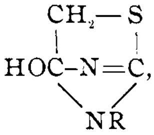
metastatic change into a labile pseudothiohydantoïn, and then into a stable isomer.



Three possible formulas, which might be assigned to the labile pseudothiohydantoïns, were considered by us, but no conclusive experimental evidence was produced that established any one of these structures:



I.



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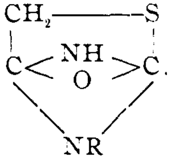

III.

The structure of the stable phenylpseudothiohydantoïn was definitely established by the fact that unsymmetrical benzylphenylthiourea and ethylchloracetate gave the same compound as was obtained by treating the stable phenylpseudothiohydantoïn with alkali and benzyl chloride, showing that the phenyl group is attached to the nitrogen outside the ring. This formula was assigned to the phenylpseudothiohydantoïn by Dixon.[1]

As we were obliged to discontinue our investigation of this interesting rearrangement on account of lack of time, we stated that we would continue the research at the opening of the next college year. The work was again taken up in this laboratory this year with the intention of examining the behavior of potassium thiocyanate with other chloracetanilides, and incidentally gaining more definite knowledge of the structure of the labile phenylpseudothiohydantoïns.

The additional chloracetanilides, which have been studied, have been chloracet-β-naphthalide, chloracet-*m*-xylidide, chloracet-*m*-nitranilide, and chloracet-*p*-bromanilide.[2] All of the products

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[1] *J. Chem. Soc.* (London), 71, 620.

[2] "Chloracetparabromanilide suggested itself as a suitable anilide to examine in connection with our work. This was assigned to Mr. H. S. Bristol for investigation, but owing to its poisonous character he was, unfortunately, compelled to stop the investigation. All of the chloracetanilides that we have examined have attacked the skin in a very disagreeable manner, producing symptoms of the same nature as 'poison ivy.' This anilide

obtained have been examined as in the previous paper,[1] in regard to their behavior towards thiolacids and alkali, and also their behavior on heating. The reactions enumerated have served to determine whether we were dealing with a thiocyanate or a labile hydantoïn.

What structure is to be assigned to the intermediate products formed in these rearrangements is still left undecided. It is a curious fact that there is no uniformity in the action of potassium thiocyanate on the different chloracetanilides. In one case it is the thiocyanate that has the greater tendency to form, while in another, it is the labile hydantoïn. Of the chloracetanilides examined in this paper not one has reacted smoothly with potassium thiocyanate, and given all the three possible products of the reaction. In the metaxylyl derivatives the thiocyanate and stable hydantoïn were the only products identified, while from chloracet-β-naphthalide the thiocyanate was missing, and only the labile and stable hydantoïns were obtained. From chloracet-*m*-nitranilide only one product was identified; this had all the properties of a labile hydantoïn.

EXPERIMENTAL PART.

BY W. K. WALBRIDGE.

Chloracet-β-Naphthalide, $ClCH_2CONHC_{10}H_7$.—This body was obtained by treating chloracetyl chloride with β-naphthylamine. It was moderately soluble in benzene, very soluble in alcohol, but insoluble in water. It is best purified by crystallizing from dilute alcohol, from which it separates in rosettes or fine needles, and melts when pure at 117°-118°. A nitrogen determination gave:

	Calculated for $C_{12}H_{10}ONCl$.	Found.
Nitrogen	6.38	6.42

Labile β-Naphthylpseudothiohydantoïn.— Chloracet-β-naphthalide and potassium thiocyanate reacted immediately when boiled in alcoholic solution. Ten grams of the chloracetnaphthalide and molecular proportions of potassium thiocyanate were boiled in 30 cc. of alcohol for ten minutes; after filtering from potassium chloride, small prisms immediately separated, which melted at 147°, after recrystallization from alcohol. A nitrogen determina-

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proved to be a most violent poison. It seemed to attack the connecting tissue beneath the skin, causing a superficial *oedema,* and thence transmitted to the blood, causing *albuminuria.* The itching did not entirely disappear for over a month."

[1] *Loc. cit.*

tion agreed with the calculated for *α-keto-μ-imino-N-β-naphthyltetrahydrothioazole.*

	Calculated for $C_{13}H_{10}ON_2S$.	Found.
Nitrogen	11.57	11.62

Several attempts were made to isolate a lower melting isomer by shortening the time of heating, and using varying quantities of alcohol, but no evidence was obtained of any body being formed here except the one isolated melting at 147°, and the stable naphthylpseudothiohydantoïn.

Action of Thioacetic Acid.—That we were dealing here with a labile hydantoïn and not with the first product of the reaction—a thiocyanate—was shown by the action of thioacetic acid. Three grams of the hydantoïn and the calculated quantity of thioacetic acid were boiled in 35 cc. of dry benzene for about two hours. Much hydrogen sulphide was evolved during the reaction. The reaction-product, which crystallized out on cooling, was purified by recrystallizing from benzene; it separated in the form of needles and melted when pure at 139°-140°. A nitrogen determination agreed with the calculated for *α keto-μ-acetimino-N-β-naphthyltetrahydrothiazole.*

	Calculated for $C_{15}H_{12}O_2N_2S$.	Found.
Nitrogen	9.86	9.76

β-Naphthylacetthiohydantoic Acid.—Accompanying the thiazole derivative described was a small amount of insoluble material, which was purified by repeatedly boiling with fresh benzene. It melted with effervescence at temperatures varying from 167° to 173° according to the rapidity of heating. The behavior on melting, its insolubility in the ordinary solvents, and a nitrogen determination identified this body as naphthylacetthiohydantoic acid.

	Calculated for $C_{15}H_{14}O_3N_2S$.	Found.
Nitrogen	9.27	9.32

Behavior on Heating: Stable β-Naphthylpseudothiohydantoïn.—The labile naphthylpseudohydantoïn showed no strong tendency to pass over into the stable isomer. After heating the dry material for several hours in a boiling water-bath unaltered material was obtained. When the hydantoïn melting at 147° was completely melted in an oil-bath, and heated for from ten to fifteen minutes at 140°-150°, a black, vitreous cake was obtained on cooling, from which the impure stable hydantoïn was obtained. A smooth rearrangement could not be obtained in this way—the decomposition products interfering with the purification of the stable hydantoïn. When the labile hydantoïn was boiled for three and one-half hours in dilute alcohol it was converted very smoothly into the stable hydantoïn, melting when pure at 213°-214°, with decomposition. A small amount of the hydantoic acid is also formed at the same time.

β-Naphthylpseudothiohydantoic Acid.—This acid was prepared by boiling, for one hour, an alcoholic solution of ammonium chloracetate and β-naphthylthiourea. The hydantoic acid separated as an amorphous body and melted with effervescence at temperatures varying from 195°-230° according to the rapidity of heating. It is insoluble in the ordinary solvents. A nitrogen determination gave:

	Calculated for $C_{13}H_{12}O_2N_2S$.	Found.
Nitrogen	10.77	10.86

Stable β-Naphthylpseudothiohydantoïn.—This hydantoïn was prepared by warming the preceding hydantoic acid on the water-bath with glacial acetic acid for four hours. Water precipitated the hydantoïn. It was difficultly soluble in benzene, but crystallized from alcohol in fine needles, and melted when pure at 213°-214°, with decomposition. A nitrogen determination gave:

	Calculated for $C_{13}H_{10}ON_2S$.	Found.
Nitrogen	11.57	11.65

This stable hydantoïn was always deposited during the spontaneous evaporation of the alcoholic filtrates in the preparation of the labile hydantoïn. We also observed that the labile hydantoïn could be converted very smoothly into the stable hydantoïn by boiling for a few minutes with strong hydrochloric acid.

Action of Alkali on the Stable Hydantoïn.—The stable hydantoïn dissolves very easily in warm sodium hydroxide solution. When cooled, the alkaline solution deposits the sodium salt of the stable hydantoïn in the form of brilliant spangles. Acetic acid precipitates again the unaltered hydantoïn.

Action of Acetic Anhydride.—When the stable β-naphthylpseudothiohydantoïn was warmed for fifteen minutes in the water-bath with an excess of acetic anhydride a thick paste was obtained; after pouring into water a thick amorphous deposit resulted, which was very soluble in alcohol, and reprecipitated by water as an oil. The product was finally obtained pure by crystallizing from benzene, from which it separated in fine needles, and melted sharply at 142°-143°. A nitrogen determination agreed with the calculated for a monoacetyl derivative, *α-keto-μ-β-naphthylimino-N-acettetrahydrothiazole.*

	Calculated for Monoacetyl— $C_{15}H_{12}O_2N_2S$.	Calculated for Diacetyl— $C_{17}H_{14}O_3N_2S$.	Found.
Nitrogen	9.86	8.59	10.27

A quantitative determination of the acetyl groups was made by saponification with standard potassium hydroxide, and titrating the excess of free alkali with standard hydrochloric acid.

Calculated for $(CH_3CO)_1$	Calculated for $(CH_3CO—)_2$.	Found.
15.14	26.37	12.52

α-Keto-β-benzilidene-μ-Naphthyliminotetrahydrothiazole.—This was obtained by warming in the water-bath, for five hours, the sodium salt of the stable hydantoïn with molecular proportions of benzaldehyde in alcoholic solution. It separated from the hot alcohol solution as pale yellow plates, and melted at 272° with slight effervescence. A nitrogen determination gave:

	Calculated for $C_{20}H_{14}ON_2S$.	Found.
Nitrogen	8.48	8.43

BY D. F. MCFARLAND.

Chloracet-m-xylidide,

$$ClCH_2CONHC_6H_3(CH_3)_2,(CH_3,CH_3,NH,1,3,4).$$

—This body was obtained by the action of chloracetyl chloride on *m*-xylidine. It crystallized from alcohol in the form of needles and melted at 151°-152° C. It is very soluble in alcohol, and moderately soluble in benzene. A nitrogen determination gave:

	Calculated for $C_{10}H_{12}ONCl$.	Found.
Nitrogen	7.09	7.26

Normal Thiocyanacet-m-xylidide, $NCSCH_2CONHC_6H_3(CH_3)_2$.—When chloracet-*m*-xylidide was boiled with a slight excess of potassium thiocyanate in alcoholic solution for twenty minutes, water precipitated from the alcoholic solution unaltered chloride. After evaporating the aqueous solution *in vacuo* a fair quantity of brilliant prisms separated, which were quite soluble in alcohol, ether, and benzene, and melted at 98°. A nitrogen determination agreed with the calculated for *thiocyanacet-m-xylidide.*

	Calculated for $C_{11}H_{12}ON_2S$.	Found.
Nitrogen	12.72	12.97

By further evaporation of the mother-liquor a white granular substance separated, which was insoluble in the ordinary solvents and melted with effervescence at about 179°. This was identified as *m*-xylylthiohydantoic acid, identical in properties with that prepared for comparison from *m*-xylylthiourea and ammonium chloracetate. We made attempts to obtain larger yields of the thiocyanate by boiling the chloracet-*m*-xylidide with potassium thiocyanate in alcoholic solution for a longer time, but while less unaltered chloride was obtained by such treatment, the amount of thiohydantoïc acid formed was increased, while the yield of thiocyanate was decreased.

Action of Thioacetic Acid.—When the thiocyanate melting at 98° was boiled with thioacetic acid in benzene solution for a few hours and then allowed to evaporate, a varnish was obtained, which dissolved immediately in cold sodium hydroxide solution. Acetic acid precipitated a mixture of the thiohydantoic acid melting at about 180°, and a yellow crystalline body which crystallized from alcohol and melted fairly sharp at 162°. Not enough of this was obtained for complete purification and analysis, but its color and solubility in alkali served to identify it as a dithiourethane.

Behavior on Heating.—This thiocyanate proved to be very stable when heated in a dry state in the boiling water-bath. After twenty-six hours' heating, it finally completely solidified to a dark red colored body; on crystallizing this from alcohol it separated in clusters of fine needles and melted at 157°, the melting-point found for the corresponding stable *m*-xylylpseudothiohydantoïn. A similar rearrangement was obtained when the thiocyanate was heated for one hour in an oil-bath at 145°. A brown mass was obtained from which was isolated the stable hydantoïn.

No indications of the formation of any intermediate labile hydantoïn were observed during these experiments. Several attempts were made to isolate a labile hydantoïn by boiling the thiocyanate in ether and benzene, but no great change in the melting-point was observed after boiling for seven or eight hours. Slight decomposition usually took place on prolonged boiling. In its behavior on heating, this thiocyanate is similar to the isomeric thiocyanacetorthoxylidide examined in a previous paper.[1]

m-Xylylthiohydantoic Acid.—This acid was made by boiling ammonium chloracetate with *m*-xylylthiourea in alcoholic solution. It separated as a fine white powder, was practically insoluble in the ordinary organic solvents, and melted with effervescence at about 179°-180°. A nitrogen determination gave:

	Calculated for $C_{11}H_{14}O_2N_2S$.	Found.
Nitrogen	11.76	12.40

Stable m-Xylylpseudothiohydantoïn.—This hydantoïn was obtained by heating the above hydantoic acid with glacial acetic acid on the water-bath. It was easily dissolved by hot alcohol, but crystallized on cooling in clusters of needles, which melted at 157°. A nitrogen determination gave:

	Calculated for $C_{11}H_{12}ON_2S$.	Found.
Nitrogen	12.72	12.52

Action of Alkali.—When the stable hydantoïn was warmed with sodium hydroxide solution it easily dissolved; on cooling, beautiful glistening plates of the sodium salt separated, which gave no definite melting-point.

Action of Acetic Anhydride.—When the stable *m*-xylylpseudothiohydantoïn was heated with acetic anhydride at 100° for about forty-five minutes a strong red colored solution resulted. Water precipitated a semi-solid which was purified by crystallizing from alcohol. It separated in granular crystals and melted at 165°-166° with slight decomposition. A nitrogen determination agreed with the calculated for a monacetyl derivative of the thiohydantoïn.

	Calculated for $C_{13}H_{14}O_2N_2S$.	Found.
Nitrogen	10.68	10.69

In respect to their behavior with acetic anhydride the stable *β*-naphthyl- and *m*-xylylpseudothiohydantoïns are to be classed by themselves in that they both gave monoacetyl derivatives. Of the stable hydantoïns discussed in a previous paper,[1] three—phenyl, orthotolyl, and paratolyl—gave diacetyl derivatives when treated in the same way.

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[1] *Loc. cit.*

By W. B. Cramer.

Chloracet-m-nitroanilide, $ClCH_2CONHC_6H_4NO_2$.—This anilide was prepared from chloracetyl chloride and *m*-nitroaniline. It crystallized from alcohol in plates and melted at 101°-102° C. A nitrogen determination gave:

	Calculated for $C_8H_7O_3N_2Cl$.	Found.
Nitrogen	13.04	13.03

Labile m-Nitrophenylpseudothiohydantoïn.—This body was obtained by boiling in benzene chloracet-*m*-nitroanilide with potassium thiocyanate for twenty minutes. It crystallized from alcohol in the form of plates and melted at 183°-184° C. A nitrogen determination gave:

	Calculated for $C_8H_7N_3O_3S$.	Found.
Nitrogen	17.79	17.60

Action of Alkali.—This hydantoïn melting at 183°-184° dissolved in cold sodium hydroxide solution. On neutralizing with acetic acid a mass of needles separated. They were purified by crystallizing from benzene and melted at 133°-134° C. A nitrogen determination agreed with the calculated for *m-nitrophenylcyanamide.*

	Calculated for $C_7H_5N_3O_2$.	Found.
Nitrogen	25.78	25.57

New Haven, Connecticut,
February 28, 1903.

[Contribution from the Chemical Laboratory of the North Carolina Department of Agriculture.]

METHODS FOR THE DETERMINATION OF TOTAL PHOSPHORIC ACID AND POTASH IN SOILS.

By C. B. Williams.

Received February 9, 1903.

Agricultural chemists have seemingly, in recent years, placed too little stress upon the determination of total plant food in soils, as a knowledge of the quantity present is necessary for a thorough understanding of the potentialities, culture methods, and fertilizer requirements of any soil, as well as entering vitally into the interpretations given availability results. With these facts in mind, the writer has, during the past summer, devoted some time to