

The greatest variation in any of the values obtained from the butter-fat is shown by the Reichert-Meissl value. In the first series of samples, the Reichert-Meissl value of the fat is higher after blowing than before, while in the second series it is just the reverse. I am unable to account for this. The variations in the other values are slight, and no definite conclusion can be drawn from them. Apparently the differences in the composition of butter-fat brought about by renovation, if any, are minute, and a long series of comparative analyses would be necessary to develop them.

For the present, reliance must be placed upon the physical tests for melted fat, as previously detailed.

I am indebted to Messrs. Simons, Adams, and Law, assistants in the laboratory, by whom the analytical work was performed.

[CONTRIBUTIONS FROM THE SHEFFIELD LABORATORY OF YALE UNIVERSITY.]

ON SOME ALDEHYDE CONDENSATION PRODUCTS OF ARYL PSEUDOTHIOHYDANTOÏNS.

BY HENRY L. WHEELER AND GEORGE S. JAMIESON.

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IN the course of our¹ work on the molecular rearrangement of thiocyanacetanilides it was found that certain stable pseudothiohydantoïns gave diacetyl derivatives when warmed with acetic anhydride, and it was shown that these acetyl compounds did not behave like acetoacetic acid derivatives. This would seem to indicate that the group $\text{—CO—CH}_2\text{—S—}$ is not present in the stable pseudothiohydantoïns.

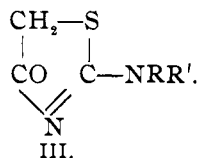
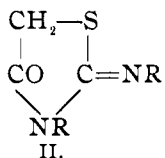
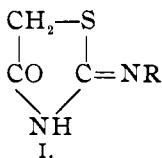
It has been shown, however, by Andreasch² that the non-substituted pseudothiohydantoïn condenses with benzaldehyde and behaves like other³ compounds which contain the above group; and we have now found that substituted pseudothiohydantoïns, which are to be represented by formulas I, II and III, are also capable of condensing with aldehydes and with oxalic ester. The stable pseudothiohydantoïns (I) therefore behave in a

¹ Wheeler and Johnson: *Am. Chem. J.*, **28**, 121 (1902).

² *Monatsh. Chem.*, **8**, 407.

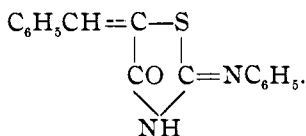
³ Loven: *Ber. d. chem. Ges.*, **18**, 3242 (1885); Nencki and Sieber: *Ibid.*, **17**, 2278 (1884); Ginsberg and Bondzynski: *Ibid.*, **19**, 119 (1886); *Monatsh. Chem.*, **8**, 358 (1887); Andreasch: *Ibid.*, **8**, 407, **10**, 75 (1889).

tautomeric manner in regard to their reactions with acetic anhydride and aldehydes.



The condensation products which we have obtained vary in color from light yellow to deep red and have the properties of weak dyes; in this they resemble the corresponding products of rhodanic acid, α - μ -diketotetrahydrothiazole, and the non-substituted pseudothiohydantoin with salicylic and cinnamic aldehydes which have been described by Andreasch and Zipser.¹

Benzaldehyde and Phenylpseudothiohydantoin,



Ten grams of the stable phenylpseudothiohydantoin were dissolved in about 150 cc. of alcohol containing 1.2 grams of sodium. To this solution 5.3 grams of benzaldehyde were added and the mixture was heated for several hours. The alcohol was then evaporated, water and dilute acetic acid were added and, after thorough stirring, the yellow precipitate was filtered, washed and dried. The yield of this crude material corresponded with the theoretical. For analysis the substance was crystallized from alcohol and from amyl acetate, whereupon, minute, slender, light yellow prisms separated from both solvents. They melted at about 251°-252°, and a nitrogen determination gave:

	Calculated for C ₁₆ H ₁₂ ON ₂ S.	Found.
Nitrogen.....	10.0	9.9

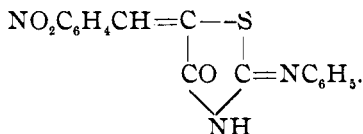
This compound or α -keto- μ -phenylimido- β -benzaltetrahydrothiazole is insoluble in water. It is fairly soluble in hot alcohol and it dissolves in hot dilute alkali but separates out again on cooling; it can be crystallized from dilute hydrochloric acid.

The *sodium ethylate addition product*, C₁₆H₁₂ON₂S.NaOC₂H₅, is readily obtained by mixing the constituents in alcoholic solu-

¹ *Chem. Ztg.*, **26**, 54, 623 (1902).

This material is difficultly soluble in alcohol and amyl acetate. It dissolves in glacial acetic acid and in hot alkali, but it is insoluble in water.

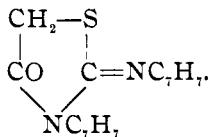
Metanitrobenzalphenylpseudothiohydantoin,



This was prepared in the same manner as the above. It was obtained as a dark brick-red crystalline powder which proved to be less soluble than the preceding compounds. For analysis it was purified by boiling with alcohol and dissolving in alkali, precipitating with acetic acid and then washing with water. Thus obtained it did not melt at 290° and a nitrogen determination gave:

	Calculated for C ₁₆ H ₁₁ O ₃ N ₂ S.	
Nitrogen.....	12.9	Found. 12.6

Diorthotolylpseudothiohydantoin,

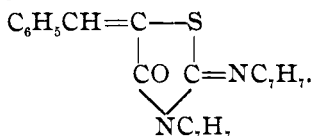


Fifty grams of diorthotolylthiurea and 20 grams of chloracetic acid were mixed in alcohol and the solution warmed for several hours. Upon cooling, colorless, flat prisms separated which, on crystallizing from alcohol, melted at 151°-152°, and a nitrogen determination gave:

	Calculated for C ₁₇ H ₁₆ ON ₂ S.	
Nitrogen.....	9.4	Found. 9.7

This hydantoin is readily soluble in alcohol and strong acetic acid but insoluble in alkali.

Benzaldiorthotolylpseudothiohydantoin,



This formed slender, light yellow prisms, when crystallized from alcohol, melting at 179° - 180° . It is readily soluble in alcohol and insoluble in alkali. A nitrogen determination gave:

	Calculated for $C_{24}H_{20}ON_2S$.	Found.
Nitrogen.....	7.29	7.65

The *sodium ethylate addition product*, $C_{24}H_{20}ON_2S \cdot NaOC_2H_5$, was obtained as a light yellow powder which did not melt at 275° . It was crystallized from alcohol and analyzed with the following results:

	Calculated for $C_{26}H_{22}O_2N_2SNa$.	Found.	
		I.	II.
Nitrogen.....	6.19	6.21	6.13

Paradimethylaminophenylthiourea,

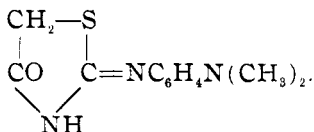
$H_2N-CS-NHC_6H_4N(CH_3)_2$, was prepared from *p*-dimethylphenylene diamine hydrochloride and ammonium thiocyanate, in the usual manner. On crystallizing from alcohol, it formed a pale yellow powder which melted with effervescence at 180° - 181° , giving a red liquid. A nitrogen determination gave:

	Calculated for $C_8H_{13}N_3S$.	Found.
Nitrogen.....	21.53	21.38

Paradimethylaminophenylthiohydantoic acid,

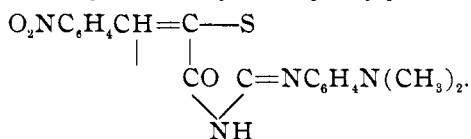
$HOCOCH_2S-C(NH)-NHC_6H_4N(CH_3)_2$, was obtained from the above by warming with alcoholic ammonium chloracetate. It separated as a light yellow, insoluble powder.

Paradimethylaminophenylpseudothiohydantoin,



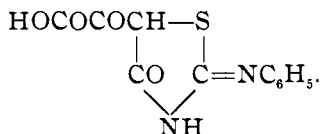
The above thiohydantoic acid was warmed with an excess of glacial acetic acid until solution took place. The acid was then neutralized with sodium carbonate and the precipitate was washed, dried and crystallized from alcohol. It formed a finely divided, dull yellow powder which sintered at about 210° and melted at 222° . A nitrogen determination gave:

	Calculated for $C_{11}H_{13}ON_3S$.	Found.
Nitrogen.....	17.87	18.20

Paranitrobenzalparadimethylaminophenylpseudothiohydantoin,

Molecular quantities of paranitrobenzaldehyde, sodium ethylate and the above hydantoin were warmed for several hours in alcoholic solution. The alcohol was then evaporated and the residue was treated with water and acetic acid; the product was a deep red powder, insoluble in water and only slightly soluble in alcohol. For analysis it was boiled with water and alcohol. It then melted at about 250°-252° and a nitrogen determination gave:

	Calculated for C ₁₈ H ₁₀ O ₃ N ₄ S.	Found.
Nitrogen	15.2	14.9

Phenylpseudothiohydantoinglyoxylic acid,

Ten grams of phenylpseudothiohydantoin, 1.2 grams of sodium, and 10 grams of ethyl oxalate were dissolved in alcohol and allowed to stand for two days. The solution was then heated to boiling for a few minutes and allowed to cool. The yellow sodium salt which separated was filtered and decomposed by dilute acetic acid. The product then crystallized from alcohol or amyl acetate in minute yellow crystals which melted, with effervescence, to a dark red liquid at about 221°-222°. A nitrogen determination gave:

	Calculated for C ₁₁ H ₈ O ₄ N ₂ S.	Found.
Nitrogen	10.6	10.7

This acid is insoluble in water and difficultly soluble in alcohol. The *silver salt* was prepared by dissolving the acid in dilute alcoholic sodium hydroxide and adding silver nitrate. It formed a slate-colored amorphous precipitate which gave the following result on analysis:

	Calculated for C ₁₁ H ₆ O ₄ N ₂ SAg ₂ .	Found.
Silver	45.1	45.2