acetic anhydride the product weighed 2.3 g. The pure substance is easily soluble in hot acetic anhydride, alcohol and carbon tetrachloride, crystallizing in each case in beautiful yellow needles. The substance melts at 200–1°.

0.1998 g. gave 0.2850 g. CO_2 and 0.0358 g. H_2O.
0.1048 g. gave 0.0915 g. AgBr.
Calc. for $C_{14}H_8O_6Br_2$: C, 38.89; H, 1.87; Br, 37.01. Found: C, 38.89; H, 1.97; Br, 37.15.

The bromine is not removed by stannous chloride in 2% hydrochloric acid as shown below.

1,4-Dihydroxy-2,3-dibromo-5,6-diacetylnaphthalene (21), $C_{10}H_{14}O_6Br_2$.—One-half gram of dibromodiacetylnaphthazarine is suspended in 15 cc. of 2% hydrochloric acid and about 5 g. of stannous chloride are added. The mixture is heated and as the yellow naphthazarine passes into solution, colorless crystals separate out. The yield amounts to a half gram. The product is insoluble in benzene and ligroin but is soluble in hot amyl alcohol, chloroform and ethyl acetate. It is best recrystallized from a large volume of hot chloroform. The pure substance consists of small colorless needles which melt to a red liquid at 196–7°.

0.1263 g. gave 0.1772 g. CO_2 and 0.0286 g. H_2O.
Calc. for $C_{14}H_{10}O_6Br_2$: C, 38.71; H, 2.32. Found: C, 38.26; H, 2.53.

This compound is isomeric with 11 but it is not a quinone. It is the only product obtained in our work which has retained its bromine after stannous chloride treatment.

CHAPEL HILL, N. C.

[CONTRIBUTION FROM THE SHEFFIELD CHEMICAL LABORATORY OF YALE UNIVERSITY, AND THE CHEMICAL LABORATORY OF MOUNT HOLYOKE COLLEGE.]

THE REDUCTION OF 4-ANISALHYDANTOIN 1-ACETIC ACID AND ITS ETHYL ESTER.

BY DOROTHY A. HAHN AND C. PAULINE BURT.
(In coöperation with TREAT B. JOHNSON.)

Received August 23, 1917.

In a previous paper from the Sheffield Laboratory[1] the fact was noted that in the reduction of 4-anisalhydantoin 1-acetic acid by means of zinc in acetic acid and by means of sodium amalgam in alcoholic solution (kept neutral by additions of acetic acid) products were encountered which showed no tendency to melt at 315° and which were convertible into the original acid. It was not possible at the time to obtain pure substances and to clear the matter up. The evidence, however, seemed to point to the possibility that we were dealing here with geometrical isomerides.

These reactions have since been made the subject of further investigation, and it has been found that in both cases of reduction salts are formed as intermediate products in the course of the reaction.

---

[1] Johnson and Hahn, THIS JOURNAL, **39**, 1263 (1917).

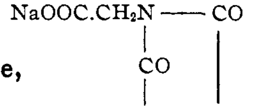
In the case of reduction by means of sodium amalgam in alcoholic solution a variety of products was obtained depending upon the conditions of the experiment. When the solution was kept neutral by additions of small quantities of acetic acid from time to time, the products were: (1) the monosodium salt of 4-anisalhydantoin 1-acetic acid—the result of boiling the mixture for one hour, and (2) the monosodium salt of 4-anisylhydantoin 1-acetic acid—the result of two hours' boiling. The monosodium salt of the unsaturated acid offered difficulties of separation and identification in that it crystallized from its aqueous solutions with water of crystallization. Starting with a pure white substance, and crystallizing from water, well-defined greenish yellow crystals were obtained. These, when air dried and analyzed, gave widely differing results. When dried in a desiccator to constant weight, and when heated, the substance suffered a change in color to white, and analyses gave results that were again constant. It was impossible to determine accurately the amount of water of crystallization because of the ease with which this was given off even with the most careful air drying.

When the ethyl ester was substituted for the free acid, the product was found to be the corresponding saturated ester. The reaction was quantitative and took place upon boiling for one hour in an alcoholic solution kept neutral by additions of acetic acid.

Reduction with sodium amalgam in alkaline solution gave the disodium salt of the saturated open-chain acid. The reaction was quantitative, and took place with ease when the mixture was boiled for one hour.

When zinc in acetic acid was used as a reducing agent, the only new product isolated was a zinc salt corresponding to the open-chain unsaturated acid with the hydrogen atoms of both acid groups apparently replaced by a single atom of zinc. The formation of this salt seemed to interfere with the further process of reduction.

Experimental Part.

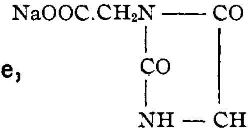


Sodium 4-Anisalhydantoin 1-Acetate, was obtained by heating 4-anisalhydantoin 1-acetic acid with sodium amalgam in alcoholic solution. 6 g. of 4-anisalhydantoin 1-acetic acid and an amount of 2% sodium amalgam corresponding to one equivalent of sodium were suspended in a mixture of 300 cc. of 95% alcohol and 50 cc. of water. The flask was connected with a return condenser and the mixture heated for one hour. Small amounts of acetic acid were added from time to time to keep the reaction neutral. At the end of the reaction the white solid in suspension was decanted from the mercury, and the mercury washed with hot alcohol. The product obtained was found to consist of a salt which did not melt at 315°. This was analyzed without further treatment.

Calc. for $C_{13}H_{11}O_6N_2Na$: N, 9.39; Na, 7.71. Found: N, 9.05, 9.11; Na, 7.68, 7.75.

The salt dissolved in water to give a greenish yellow solution. In recrystallizing from hot water the substance separated upon cooling in the form of well-defined greenish yellow plates. These were dried in air. The results of analyses of the compound showed great variation. It was observed that on standing in the air and also upon heating, the substance suffered a change in color to white, and it was concluded that this might be due to a loss of water of crystallization. Experiments showed that when dried in a desiccator the substance lost in weight, and that when dried to constant weight, the results no longer showed any variation, but corresponded with the value calculated for a monosodium derivative of 4-anisalhydantoin 1-acetic acid.

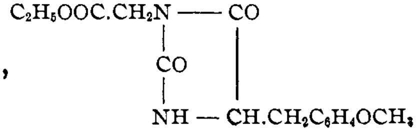
The aqueous solution when acidified with hydrochloric acid gave a precipitate. This was filtered, washed and dried. It melted at 271° and was identified as 4-anisalhydantoin 1-acetic acid by comparison with an analyzed sample.



Sodium 4-Anisylhydantoin 1-Acetate, was obtained by heating 4-anisalhydantoin 1-acetic acid with sodium amalgam in alcoholic solution. The flask was connected with a return condenser and the mixture heated for two hours. Small amounts of acetic acid were added to keep the reaction neutral. At the end of the reaction the clear solution was filtered from the mercury and the mercury washed with a little hot alcohol. On standing overnight, a white substance crystallized out. This was filtered and washed with a little alcohol. It was only slightly soluble in alcohol and recrystallized from alcohol in needles. It did not melt at 300°.

Calc. for $C_{13}H_{13}O_5N_2Na$: Na, 7.66. Found: Na, 6.91, 6.97.

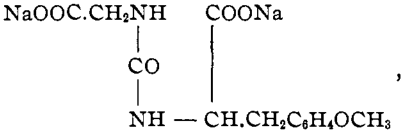
An aqueous solution of the substance when acidified with hydrochloric acid gave a precipitate. This was filtered, washed and dried. It melted at 166° and was identified as 4-anisylhydantoin 1-acetic acid by comparison with an analyzed specimen.



Ethyl 4-Anisylhydantoin 1-Acetate,

was formed by treating ethyl 4-anisalhydantoin 1-acetate with sodium amalgam in alcohol solution. 6 g. of ester and an excess of sodium amalgam were suspended in a mixture of 300 cc. of 95% alcohol and 30 cc. of water, and the mixture was connected with a return condenser and heated for one hour. At the end of that time the clear hot solution was filtered from the mercury. The filtrate was then concentrated to one-half its volume, and allowed to cool. The crystalline product was filtered and washed with cold alcohol. It melted sharply at 138° and was identified by comparison with an analyzed specimen. The yield was quantitative.

Disodium *p*-Methoxyphenylalanine-glycine Urea,



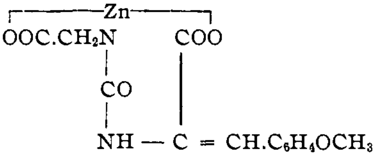
$$\begin{array}{ll} \mathrm{NaOOC.CH_2NH} & \mathrm{COONa} \\ \quad | & | \\ \quad \mathrm{CO} & | \\ \quad | & | \\ \multicolumn{2}{l}{\quad \mathrm{NH - CH.CH_2C_6H_4OCH_3}} \end{array}$$

, was obtained by heating 4-anisalhydantoin 1-acetic acid with an excess of sodium amalgam in dilute alcohol. 6 g. of acid and an excess of sodium amalgam were suspended in a mixture of 300 cc. 95% alcohol and 30 cc. of water. The mixture was connected with a return condenser and heated for one hour. At the end of that time the solution, containing a finely divided white solid in suspension, was decanted from the mercury and the mercury washed with hot alcohol. The solution was filtered hot, and the precipitate washed with alcohol. The product obtained in this way was found to consist of a salt which did not melt at 300°. It was purified by dissolving in water and precipitating with alcohol-ether mixtures. The yield was quantitative.

Calc. for $C_{13}H_{14}O_6N_2Na_2$: N, 8.23; Na, 13.53. Found: N, 7.77, 7.64; Na, 13.10, 13.07.

The substance was very soluble in water and soluble in alcohol. It was also readily soluble in acetic acid, and could be precipitated unchanged from this solvent by the addition of ether. When dissolved in water and the solution carefully acidified in the cold with hydrochloric acid, it passed into the corresponding open-chain acid which melted at 166° with an effervescence of gas. The identity of this acid was established by comparison with an analyzed specimen.

A Derivative of 4-Anisalhydantoin 1-Acetic Acid Containing One Atom of Zinc for one equivalent of acid and corresponding to the formula,



$$\begin{array}{ll} \multicolumn{2}{c}{\ulcorner\text{———}\mathrm{Zn}\text{———}\urcorner} \\ \mathrm{OOC.CH_2N} & \mathrm{COO} \\ \quad | & | \\ \quad \mathrm{CO} & | \\ \quad | & | \\ \multicolumn{2}{l}{\quad \mathrm{NH - C = CH.C_6H_4OCH_3}} \end{array}$$

, was formed when the acid was heated with zinc in aqueous acetic acid. 2 g. of 4-anisalhydantoin 1-acetic acid and small amounts of powdered zinc were suspended in a mixture of 20 cc. of acetic acid and 15 cc. of water. The mixture was heated in an open flask on a steam bath for 11 days. More zinc was added from time to time, also small amounts of acetic acid and water. At the end of the reaction, the clear, hot solution was filtered. Cold water was added, and a heavy precipitate immediately formed. This was filtered and washed with a little cold water. The precipitate was extracted with hot water several times to remove all traces of zinc acetate. It was then extracted with alcohol. It was only slightly soluble in water, and was recrystallized from large amounts of water.

Calc. for $C_{13}H_{11}O_6N_2Zn$: N, 7.84. Found: 7.87.

The presence of zinc in the compound was confirmed by qualitative tests for the metal. A small amount of the salt was placed in a porcelain crucible, moistened with a few drops of nitric acid, and heated carefully to avoid spattering. The residue was yellow and insoluble in water. This was treated with hydrochloric acid and evaporated to dryness. The white residue was soluble in water. When ammonium sulfide was added to the aqueous solution, zinc sulfide was formed as a white precipitate.

The salt was much more soluble in aqueous ammonia than in pure water. Its ammoniacal solution when acidified precipitated a substance melting at 271° which was identified as the original acid.

Conclusion.

The high-melting products which are formed when 4-anisalhydantoin 1-acetic acid is treated with sodium or zinc in reducing media have been identified as the respective salts of this acid. The result disproves conclusively our previous supposition that these substances in both cases might be the geometrical isomeride of the unsaturated acid.

SOUTH HADLEY, MASS.

[CONTRIBUTION FROM THE LABORATORIES OF THE OFFICE OF SOIL FERTILITY, BUREAU OF PLANT INDUSTRY, U. S. DEPARTMENT OF AGRICULTURE.]

THE IDENTITY OF CYANURIC ACID WITH SO-CALLED "TETRACARBONIMID."

BY E. H. WALTERS AND LOUIS E. WISE.

Received August 20, 1917.

In a recent publication dealing with the isolation of cyanuric acid from soil, the authors[1] pointed out the striking similarity between the properties of cyanuric acid and those of the so-called "tetracarbonimid" obtained by Scholtz[2] as a product of the oxidation of uric acid with alkaline hydrogen

---

[1] Louis E. Wise and E. H. Walters, "Isolation of Cyanuric Acid from Soil," *J. Agr. Res.*, **10**, 85–92 (1917).

[2] M. Scholtz, "Ueber ein neues Oxydationsprodukt der Harnsaüre," *Ber.*, **34**, 4130 (1901).