direct sunlight. The crystalline mass gave, by recrystallization from chloroform or from absolute alcohol, needles melting at 132°. Calculated for $C_9H_7N.C_2I_4$: I, 76.84; found, 76.79. With water *quinolinetetraiodoethylene* yields tetraiodoethylene and quinolinehydroiodide.[1]

Other Bases.—Pyridine gave a slow-forming, dark-colored precipitate difficultly soluble in chloroform; triphenylphosphine, a white granular sticky precipitate melting at 115°; triethylstibine, white crystals; paraphenylenediamine, a blue-black precipitate; collidine, an immediate precipitate; picoline, coarse dark crystals. The following substances gave no recognizable reaction-products: PCl_3, $AsCl_3$, $SbCl_3$, AsI_3, CH_3AsH_2.

Acetamide.—Golden rhombic flakes, melting at 175°. Calculated for $CH_3CONH_2.C_2I_4$: I, 85.94; found 85.63. This and otner products formed by the action of tetraiodoethylene on organic bases will be investigated.

SEATTLE, WASH.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MICHIGAN.]

THE FORMATION OF METATHIAZINES FROM THIOUREA.[2]

BY WILLIAM J. HALE AND HARVEY C. BRILL.

Received January 22, 1912.

In a recent publication[3] the condensation of urea with nitromalonic aldehyde was shown to give a nitrohydroxypyrimidine as a final product. A comparison of this reaction with condensations where an amino-imino grouping about a central carbon atom could be brought into reaction with this same aldehyde led to the conclusion that this latter grouping was far more reactive in the formation of pyrimidines than the β-diamino grouping in urea.

When thiourea is substituted for urea in this connection, we naturally were led to expect a pyrimidine containing a mercapto group as a substituent in place of the hydroxyl group of that product obtained from urea. The condensation, however, has been found to proceed in a totally different manner.

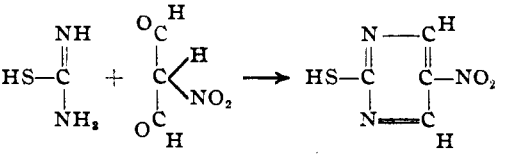
It is well known that thiourea may exist in two isomeric forms, the normal and the pseudo. Granting that the presence of the two amino groups in the normal form ($S : C : (NH_2)_2$) does not offer the favorable configuration which the amino-imino grouping of the pseudo form ($HS.C(:NH)NH_2$) has been found to give for pyrimidine formation, it would follow that we should have from this pseudo form a direct and

[1] Trowbridge, THIS JOURNAL, 21, 67.

[2] The work described in this article formed part of a thesis presented to the Faculty of the Department of Literature, Science and the Arts of the University of Michigan for the degree of Doctor of Philosophy, by Harvey C. Brill.

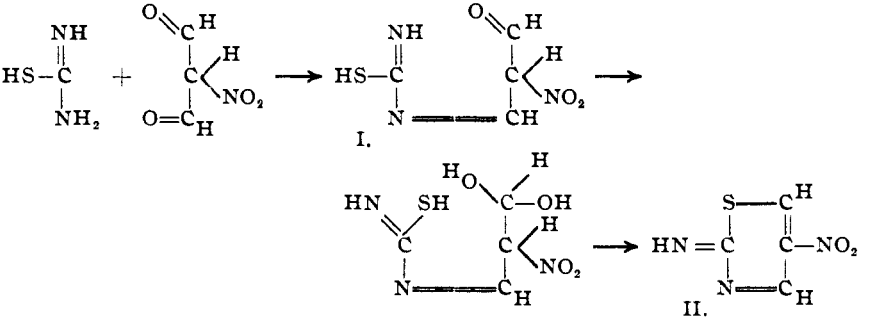
[3] THIS JOURNAL, **34**, 82 (1912).

simple condensation with nitromalonic aldehyde to give a nitromercapto-pyrimidine. The reaction may be indicated as follows:



This type of compound, however, is not produced, but in its stead a compound containing the sulfur atom in the ring. In other words when the amino group of pseudothiourea has condensed with one aldehyde group of nitromalonic aldehyde the second aldehyde group, in hydrated form, enters preferably into reaction with the mercapto group of the thiourea rather than with the imino group. This latter group was indeed found most reactive toward the formation of pyrimidines from amidines. And in this case, as one may expect, we have a condensation which runs just as readily and with good yield.

The compound obtained is in structure a six-membered ring containing one nitrogen atom meta to a sulfur, namely, a metathiazine. The intermediate product has been shown to be a monothioureide of nitromalonic aldehyde (I) as indicated below:



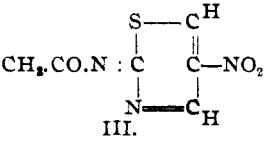
When thiourea and nitromalonic aldehyde are brought together in aqueous solution in the presence of a very small quantity of sodium hydroxide or diethylamine, the condensation proceeds only to the formation of the monothioureide, a yellow semi-crystalline substance removed by acidification of the reaction mixture. When piperidine is employed as the condensing agent the reaction proceeds further with the production of a large quantity of metathiazine, which comes out in a mass of yellow needles. The mother liquor, however, from these crystals still retains a small quantity of the thioureide, which can be removed as before stated by acidification. Condensation in presence of acids gives no well defined product, owing to the decomposition which nitromalonic aldehyde is prone to undergo.

The monothioureide of nitromalonic aldehyde is shown to have but one aldehyde group, since with phenylhydrazine it gave a monophenylhydrazone. When the monothioureide is suspended in alcohol and piperidine added, the substance slowly dissolves and undergoes a transformation into the metathiazine which precipitates immediately. There remains no doubt as to the structure of the monothioureide and its intermediate position in the formation of the metathiazine (II).

The quantity of piperidine here employed as a condensing agent has considerable to do with the yield of metathiazine. There is no combination, however, between piperidine and the final product. The metathiazine is not soluble in alkali. On continued heating with sodium hydroxide solution decomposition slowly takes place and the presence of nitromalonic aldehyde may be detected in certain cases. Upon warming this metathiazine with a basic lead acetate solution, or with mercuric oxide, no desulfurization was accomplished, thus showing the stability of the compound and the ring position of the sulfur.

When the monothioureide was subjected to treatment with basic lead acetate solution or mercuric oxide, desulfurization ensued immediately as may well be expected. The presence of the free imino group in this monothioureide was qualitatively shown by the reaction with benzene sulfochloride (Hinsberg's test) which gave the characteristic oily mass.

The presence of the imino group as a substituent in the metathiazine compound was also shown by the formation of a characteristic oily substance upon the addition of benzene sulfochloride. By action of acetic anhydride only a mono acetyl derivative of this metathiazine could be obtained. This at once proves the presence of only one replaceable hydrogen atom, basic in nature, and confirms also the structure already assigned. The compound formed is, therefore, a β-nitro-μ-acetyliminometathiazine (III):



III.

The structure of the monothioureide is further substantiated by the fact that a sulfoether is readily prepared from it by the action of dimethyl sulfate. A number of salts were also prepared. The potassium salt indicates three replaceable hydrogen atoms per molecule of monothioureide.

Thiourea has thus been found to condense in its pseudo form with a β-dialdehyde. Similar condensations, in which pseudomethyl- and pseudoethyl-thiourea were employed, have been investigated by Wheeler and

Merriam.[1] The first step in the condensation with thiourea led to a monothioureide, also shown to exist in its pseudo form. Consequently we may conclude that the presence of the imino group in this intermediate product is indicative of the manner in which these condensations must run—namely, first, by condensation between aldehyde and amino group, and second, in formation of ring, by loss of water between the mercapto and one hydroxyl group of the hydrated aldehyde.

Experimental Part.

Monothioureide of Nitromalonic Aldehyde, $C_4H_5O_3N_3S$.—Equimolecular quantities of sodium nitromalonic aldehyde and thiourea were brought together in aqueous solution and a few drops of diethylamine added. The solution (which should be somewhat concentrated) soon acquired a deep red color. After 24 hours the reaction-mixture was just acidified with dilute sulfuric acid and the yellow flocculent precipitate filtered off. This same product may be obtained when sodium hydroxide is used as the condensing agent but in poorer yields. The yield in the case just described is very good. Quantitative results are precluded by reason of decomposition products and then again by the solubility of the thioureide in slightly acid solutions. The purification of this monothioureide is accomplished by crystallization from glacial acetic acid. When carefully carried out the product separates in beautiful glistening yellow leaflets melting at 206–7° (cor.). It is soluble in acetic acid; slightly soluble in alcohol, acetone or acetic ester; insoluble in water, benzene, carbon disulfide, ether or ligroin. Its alkaline solution is readily desulfurized by gentle warming with either lead acetate or mercuric oxide.

0.1400 gram substance; 0.1420 gram CO_2; 0.0441 gram H_2O. 0.0776 gram substance; 17.22 cc. moist N (23° and 740 mm.). 0.3112 gram substance; 0.4094 gram $BaSO_4$.

Calculated for $C_4H_5O_3N_3S$:	C, 27.42;	H, 2.88;	N, 24.01;	S, 18.31.
Found:	C, 27.67;	H, 3.52;	N, 24.22;	S, 18.06.

The sulfur in this compound was determined by the sodium peroxide method.

Potassium Salt of Monothioureide of Nitromalonic Aldehyde, $C_4H_2O_3N_3SK_3$.—This salt was prepared by adding to an aqueous suspension of thioureide just sufficient potassium hydroxide solution (1:5) for complete neutralization. From the deep red solution thus formed the long, flat, reddish brown crystals of the potassium salt separated upon spontaneous evaporation. The air-dried salt contains no water of crystallization.

0.3090 gram dried salt; 0.2815 gram K_2SO_4. Calculated for $C_4H_2O_3N_3SK_3$: K, 40.63; found, 40.89.

This would indicate that not only the mercapto and the isonitroso groups but also the imino group suffered a replacement of hydrogen for potas-

[1] *Am. Chem. J.*, **29**, 478 (1903).

sium. A lead salt of this monothioureide was also prepared by careful action of lead acetate upon a solution of the potassuim salt. Its analysis, however, was vitiated owing to the great ease with which lead sulfide split off from the molecule.

Methyl Ether of Monothioureide of Nitromalonic Aldehyde, $C_4H_4O_3N_3.SCH_3$.—The action of methyl iodide upon the sodium or potassium salt of the monoureide suspended in alcohol met with little success, as only a very small yield of ether could be obtained. When, however, an aqueous solution of the potassium salt is shaken with dimethylsulfate, the methyl ether of the monothioureide is thrown out from the comparatively cold solution in a few minutes. The formation of this flocculent precipitate of the methyl ether is accompanied also by the disagreeable mercaptan odor. It is purified by crystallization from ether, from which it separates in yellow plate-like crystals m. 78–9° (cor.). It is soluble in benzene, ether or alcohol, but insoluble in water. It is fairly stable, melting and remelting at 78°.

0.0648 gram substance; 14.05 cc. moist nitrogen (24° and 720 mm.). Calculated for $C_5H_7O_3N_3S$: N, 22.21; found, 22.50.

This methyl ether is not desulfurized by action of basic lead acetate solution.

When the monothioureide and phenylhydrazine acetate are brought together in alcoholic solution the monophenylhydrazone of this monothioureide is formed. The product may be removed by the addition of water to the deep red alcoholic solution, but owing to its noncrystalline character complete purification was not effected.

β-Nitroiminometathiazine, $C_4H_3O_2N_3S$.—Equimolecular quantities of thiourea and sodium nitromalonic aldehyde were brought together in somewhat concentrated aqueous solution and a few drops of piperidine added as a condensing agent. The solution took on a deep red color immediately, and in the course of an hour long, slender, yellow needles of the metathiazine made their appearance. The reaction may be considered at an end in 24 hours. After removal of the product the alkaline mother liquor was just acidified with dilute acid, upon which a fair amount of the yellow monothioureide of nitromalonic aldehyde was precipitated. This mother liquor left after the removal of the metathiazine compound has constituted the principal source of the monothioureide for the present work.

β-Nitroiminometathiazine crystallizes from alcohol in beautiful, long, yellow needles m. 151–2° (cor.). It is readily soluble in acetone or benzene; fairly soluble in alcohol, acetic acid or acetic ester; only slightly soluble in water.

Calculated for $C_4H_3O_2N_3S$:	C, 30.35; H, 1.91; N, 26.57; S, 20.27.
Found:	C, 30.21; H, 2.34; N, 26.90; S, 20.35.

This thiazine is very stable towards both acids and alkalies. It may be crystallized from hot, concentrated hydrochloric acid without decomposition. Prolonged boiling with concentrated alkali slowly breaks up the molecule. A boiling alkaline solution of lead acetate or mercuric oxide is without effect upon it, thus indicating the firmness with which the sulfur is held in the ring. Phenylhydrazine and aniline do not react with the compound, as may be expected now that the free aldehyde group of the monothioureide has become involved with the mercapto group in a ring closing. The action of benzenesulfochloride upon the thiazine gave, upon warming, a yellow oily mass which confirms the presence of the imino group (Hinsberg's test).

β-Nitroacetyliminometathiazine, $C_4H_2O_2N_3S.(COCH_3)$.—The β-nitroiminometathiazine was warmed with an excess of acetic anhydride for an hour at a temperature of about 50° and the solution then poured into cold water. An oil is first precipitated; this, however, by stirring and a few minutes' standing, passed over into a yellow, semi-crystalline precipitate. The product was purified by crystallization from alcohol and melted at 141° (cor.). It is readily soluble in alcohol, acetone, benzene, acetic ester or carbon tetrachloride; fairly soluble in ligroin or acetic acid; slightly soluble in water, but insoluble in ether.

Calculated for $C_6H_5O_3N_3S$: N, 21.10; S, 16.42; found, 21.24, 16.11.

This acetyliminometathiazine is a fairly stable compound. It is easily hydrolyzed, however, by boiling water and yields again the free metathiazine. The production of only a monoacetyl derivative is in exact accord with the structure of the metathiazine as already shown.

ANN ARBOR, MICH.

[CONTRIBUTION FROM THE NEVADA AGRICULTURAL EXPERIMENT STATION.]

ALFALFONE, A KETONE OF THE FORMULA $C_{21}H_{42}O$, OBTAINED FROM ALFALFA. ALFALFA INVESTIGATION. II.

BY C. A. JACOBSON.

Received January 13, 1912.

When air-dried alfalfa meal is extracted with hot, 95% alcohol, and the extract allowed to cool, a heavy green precipitate settles out. By filtering, drying and extracting this precipitate with ether, according to the method given in my preliminary paper,[1] a light, fluffy powder results, which serves as the starting point for the present investigation.

About 0.5 gram of this powder together with 150 cc. nitric acid of 1.104 sp. gr. are put into a flask, connected with a reflux condenser and heated on the water bath for about two working days, or until the oily globule floating on top of the acid becomes perfectly transparent. Upon cooling the solution to the room temperature, the globule solidifies into

[1] THIS JOURNAL, 33, 2048.