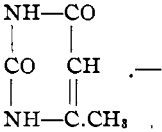
of silver in solution precipitated as sulfide by hydrogen sulfide. The solution was then boiled to remove all free hydrogen sulfide and the silver sulfide separated by filtration. The sulfuric acid was then separated by precipitation as sulfate with barium hydroxide and the excess of barium precipitated as carbonate by saturating the solution with carbon dioxide. The neutral solution was then concentrated and cooled, when the nucleoside separated in prismatic crystals. This pyrimidine was purified for analysis by crystallization from hot water and separated on cooling, in small plates. They did not possess a sharp melting point. On heating in a capillary tube the pyrimidine began to show signs of melting at about 240° and then decomposed quite sharply a 254°. This decomposition point varies according to the rate of heating. The yield of purified nucleoside was 0.6 g.

Calc. for $C_5H_6O_3N_2$: N, 19.72. Found: N, 19.42.

The structure of this nucleoside was established by its behavior on reduction with hydriodic acid.

The Formation of 4-Methyluracil,



$$\begin{array}{ll}\text{NH}—&\text{CO}\\ | & | \\ \text{CO} & \text{CH}\\ | & \| \\ \text{NH}—&\text{C.CH}_3\end{array}$$

.—Five-tenths of a gram of the nucleoside was dissolved in 15 cc. of hydriodic acid (sp. gr. 1.7) and about 0.1 g. red phosphorus added to the solution. The solution was then boiled for 4 hrs., diluted with water and finally filtered to remove the phosphorus. The halogen and phosphate radicals were then removed by digesting with an excess of silver carbonate. After filtering, the excess of silver was then precipitated as sulfide with hydrogen sulfide and the aqueous solution then decolorized by boiling with bone-coal. The solution was then concentrated and cooled, when 4-methyluracil deposited in colorless crystals. It was purified by recrystallization from hot water. It did not melt or undergo decomposition below 300° and when mixed with pure 4-methyluracil this behavior, on heating, was not altered.

Calc. for $C_5H_6O_2N_2$: N, 22.22. Found: N, 21.9.

NEW HAVEN, CONN.

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

THE ACTION OF MONOCHLOROACETIC ACID ON SEMICARBAZIDE AND HYDRAZINE.

BY J. R. BAILEY AND W. T. READ.

Received June 8, 1914.

Introduction.

Hydrazine derivatives have been prepared by the action of monochloroacetic acid on phenylhydrazine,[1] and on hydrazine,[2] but no inves-

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[1] *Ber.*, **28**, 1231 (1895); **36**, 3887 (1903).

[2] *J. prakt. Chem.*, [2] **83**, 249 (1861).

tigation of a similar reaction has been published between semicarbazide and halogen acids. Our work on this latter reaction has shown that both semicarbazinoacetic acid, $NH_2CONHNHCH_2COOH$, and semicarbazinodiacetic acid, $NH_2CONHN(CH_2COOH)_2$, result when potassium chloroacetate and semicarbazide are heated in aqueous solution. The yield of semicarbazinoacetic acid, as obtained by us, is poor, but semicarbazinodiacetic acid is readily prepared by this method. It was observed that monochloroacetic acid reacts much more easily with semicarbazide than do the halogen derivatives of the higher fatty acids, a behavior wherein semicarbazide resembles hydroxylamine.

The study of the action of potassium chloroacetate on semicarbazide suggested a modification of the method of Curtius and Hussong[2] for obtaining hydrazinodiacetic acid, which has led to a simplification of their process with a greatly increased yield. This interesting substance is now available in any amount desired with a few hours' work. Curtius and Hussong employed 5 mols of hydrazine hydrate to 2 mols of monochloroacetic acid, whereas in reality the molecule of hydrazinodiacetic acid is built from one molecule of hydrazine and two molecules of monochloroacetic acid. In their process, one molecule of this excess of hydrazine reacts to neutralize the hydrochloric acid liberated in the reaction, and a second molecule gives with the hydrazinodiacetic acid formed a hydrazine salt. The reactions that take place in the process may be interpreted as follows: $5NH_2NH_2 + 2CH_2ClCOOH = NH_2N(CH_2COOH)_2.NH_2NH_2 + NH_2NH_2.2HCl + 2NH_2NH_2$ excess. The excess hydrazine, as well as the hydrazine forming a salt with the hydrazinodiacetic acid, is removed here by fractional precipitation with benzaldehyde. Hydrazinodiacetic acid itself does not react with aldehydes. It is simply freed from the hydrazine salt by the action of the aldehyde and separates along with benzalazine, and the latter is removed by alcohol. In the modification of this process, as worked out by us, 1 mol of hydrazine hydrate, 2 mols of $CH_2ClCOOH$ and 2 mols of K_2CO_3 are employed, the reaction proceeding as follows:

$$NH_2NH_2 + 2CH_2ClCOOH + 2K_2CO_3 = NH_2N(CH_2COOK)_2 + 2KCl + 2CO_2 + 2H_2O.$$

At the end of the reaction, the hydrazinodiacetic acid is liberated from its salt by neutralization with hydrochloric acid, whereupon the hydrazine acid crystallizes out. This method is similar to the one employed by M. Busch in the preparation of asymmetric phenylhydrazinoacetic acid, $C_6H_5N(CH_2COOH)NH_2$, from 1 mol phenylhydrazine, 1 mol monochloroacetic acid, and 1 mol potassium carbonate.[3] Curtius obtained from 50

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[1] *Ann.*, **289**, 285 (1896).

[2] *J. prakt. Chem.*, [2] **83**, 271 (1861).

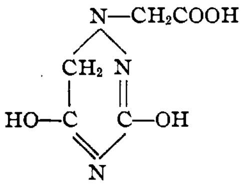
[3] *Loc. cit.*

g. hydrazine hydrate 16–18 g. of hydrazinodiacetic acid, which he reports as a 51–57% yield, but it should be observed that this calculation is based on the amount of monochloroacetic acid used (40 g.). Calculated the other way, the yield dwindles to 10.8–12.2%. We obtained from 21 g. of hydrazine hydrate 21.5 g. of recrystallized hydrazinodiacetic acid, which represents a yield of 34.6%, calculated on the basis of the hydrazine hydrate used.

Two methods were investigated for isolating semicarbazinodiacetic acid from the salt mixture formed in its preparation. The method that gave the best yield was esterification with alcoholic hydrochloric acid. As semicarbazinodiacetic acid forms a very difficultly soluble barium salt, an attempt was made to utilize this salt in the isolation of the semicarbazinodiacetic acid, but the method was not perfected to the point where the yield was equal to that in the esterification process.

The esters of semicarbazinodiacetic acid are readily oxidized with permanganate or bromine. The oxidation results in the elimination of one acetic acid rest, with the formation of esters of the semicarbazone of glyoxylic acid, $NH_2CONHN = CHCOOH$. The ethyl ester of this semicarbazone was first prepared by Simon and Chavenne.[1] Their description of the substance does not agree with the properties of the semicarbazone as determined by us. However, the constitution of the oxidation product of ethyl semicarbazinodiacetate was established beyond question by its formation, (*a*) on esterification of glyoxylic acid semicarbazone, and (*b*) on oxidation of ethyl semicarbazinomonoacetate. Furthermore, on reduction with sodium amalgam, according to the method of Darapsky and Prabhaker,[2] the oxidation product of ethyl semicarbazinodiacetate gave semicarbazinoacetic acid, $NH_2CONHNHCH_2COOH$, which was isolated by esterification. The ethyl ester obtained in this way proved identical in its properties with the semicarbazinoacetic ester prepared by Traube from the hydrochloride of ethyl hydrazinoacetate and potassium cyanate.[3]

With sodium alcoholate, the esters of semicarbazinodiacetic acid, analogous to esters of semicarbazino acids in general,[4] condense to esters of 3,5-dioxy-1,6-dihydro-1,2,4-triazine-1-acetic acid,



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[1] *Compt. rend.*, **143**, 1906 (1906).

[2] *Ber.*, **45**, 2625 (1912).

[3] *Ibid.*, **31**, 164 (1898).

[4] *Am. Chem. J.*, **28**, 386 (1902).

Boiled with the calculated amount of alkali, the esters of semicarbazinodiacetic acid are readily saponified to semicarbazinodiacetic acid; but, if heated under pressure at 150° with potassium hydroxide, semicarbazinodiacetic acid readily loses the carbonamide rest with the formation of hydrazinodiacetic acid,

$$NH_2CONHN(CH_2COOH)_2 + 3KOH = NH_2N(CH_2COOK)_2 + KHCO_3 + H_2O.$$

The constitution of hydrazinodiacetic acid and semicarbazinodiacetic acid was established conclusively by the action of sodium nitrite on hydrazinodiacetic acid and on methyl semicarbazinodiacetate, in which reactions iminoacetic acid, $NH(CH_2COOH)_2$, and methyliminodiacetate, respectively, are readily formed and proved identical with the same preparations as described by other investigators. Curtius and Hussong tried the action of nitrous acid on hydrazinodiacetic acid, but did not succeed in isolating iminodiacetic acid. The behavior of hydrazino- and semicarbazino-diacetic acids towards nitrous acid is analogous to that of asymmetric methylphenylhydrazine, $NH_2N(CH_3)C_6H_5$,[1] and diethylsemicarbazide, $NH_2CONHN(C_2H_5)_2$,[2] towards nitrous acid. The following equations interpret the reactions that take place between nitrous acid and the above hydrazine derivatives of acetic acid:

$$NH_2N(CH_2COOH)_2 + HNO_2 = NH(CH_2COOH)_2 + H_2O + N_2O$$

$$NH_2CONHN(CH_2COOCH_3)_2 + HNO_2 = NH(CH_2COOCH_3)_2 + N_2O + CO_2 + NH_3$$

Curtius and Hussong found that hydrazinodiacetic acid very readily decomposes on heating with mineral acids, in that half of the nitrogen in the molecule is eliminated as ammonia. In addition to confirming this observation, we were able to isolate among the reaction products glycocoll and nitrilotriacetic acid, $N(CH_2COOH)_3$. The primary organic complex of the hydrolysis of the hydrazine acid is assumed by Curtius and Hussong to be hydroxylaminodiacetic acid. The formation of glycocoll from hydroxylaminodiacetic acid may be explained by assuming the elimination of a molecule of water and the subsequent hydrolysis of the resulting products as follows:

$$HON(CH_2COOH)_2 = (CH_2COOH)N = CHCOOH + H_2O.$$

$$(CH_2COOH)N = CHCOOH + H_2O = NH_2CH_2COOH + CHOCOOH.$$[3]

It may be that a second form of hydrolysis proceeds along with the one suggested above in that a part of the hydrazinoacetic acid breaks down into glycollic acid and hydrazinomonoacetic acid as primary decomposition products,

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[1] *Ann.*, 190, 158 (1878).

[2] *Ibid.*, 199, 314 (1879).

[3] Cf. *Ber.*, 39, 2566 (1906).

$$NH_2N(CH_2COOH)_2 + H_2O = NH_2NHCH_2COOH + CH_2OHCOOH.$$

The interaction of glycollic acid and glycocoll could then explain the formation of nitrilotriacetic acid,

$$2CH_2OHCOOH + NH_2CH_2COOH = N(CH_2COOH)_3 + 2H_2O.$$

The assumption that glycollic acid is an intermediary product in the action of sulfuric acid on hydrazinodiacetic acid harmonizes with the behavior of semicarbazinodiacetic acid esters toward oxidizing agents, which, as shown above, results in the elimination of an acetic acid rest without a severance of the two nitrogen atoms in the original hydrazine complex.

The formation of nitrilotriacetic acid in the interaction of sulfuric acid and hydrazinodiacetic acid was quite unexpected, because Heintz found that nitrilotriacetic acid, heated with concentrated hydrochloric acid for 17 hrs. at 190° to 200°, was converted to iminodiacetic acid.[1]

However, a repetition of our experiment with hydrazinodiacetic acid gave the same uniform result. Attention might be called to the fact that this elimination of an acetic acid rest from nitrilotriacetic acid by hydrolysis, as observed by Heintz, is also strictly analogous to the second form of hydrolysis suggested above for hydrazinodiacetic acid.

In confirming the constitution of the oxidation product of ethyl semicarbazinodiacetate, as described above, the semicarbazone was reduced with sodium amalgam, according to the method of Darapsky and Prabhaker, and in this way semicarbazinoacetic acid resulted. These investigators do not isolate in their process the semicarbazino acid as such, but convert it to the hydrazino acid by the action of concentrated hydrochloric acid, and isolate the hydrazine in the form of the hydrochloride of the ethyl ester, $HCl.NH_2NHCH_2COOC_2H_5$. We discovered that semicarbazinoacetic acid itself is readily esterified and likewise forms a hydrochloride difficultly soluble in alcohol, so that an excellent method of preparing semicarbazino acids is suggested.

As shown in the experimental part of this article, this method may be used to prepare semicarbazinopropionic acid, $NH_2CONHNHCH(CH_3)COOH$, from the semicarbazone of pyruvic acid,

$$NH_2CONHN = CH(CH_3)COOH.$$

Besides Darapsky and Prabhaker, Emil Fischer,[2] Elbers,[3] and later Kessler and Rupe,[4] have effected the reduction of the N = C complex in hydrazones with sodium amalgam.

The ethyl ester of semicarbazinoacetic acid reacts with mustard oils to form thiohydantoins.[5] With benzoyl chloride, the ester gives a benzoyl

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[1] *Ann.*, **149**, 88 (1869).

[2] *Ber.*, **16**, 2241 (1883).

[3] *Ann.*, **227**, 354 (1885).

[4] *Ber.*, **45**, 26 (1912).

[5] THIS JOURNAL, **26**, 1006 (1904).

derivative, which, with alkali, loses a molecule of water with the formation of a triazol.[1] The semicarbazino ester further condenses with sodium alcoholate to the sodium salt of 3,5-dioxy-1,6-dihydro-1,2,4-triazine.[2] The hydrochloride of the ester yields, with sodium nitrite, a beautifully crystallizing nitroso derivative.

The isolation of nitroso-derivatives of semicarbazino acids extends the analogy between the semicarbazino acids and secondary amines, which show a like behavior toward acid chlorides, mustard oils, isocyanates, nitrous acid, and diazonium salts,[3] as has been demonstrated by investigations carried out in this laboratory. It is the α-nitrogen in the semicarbazino acids to which is joined the reactive hydrogen, just as in the case of phenyl semicarbazide.

Experimental Part.

Preparation of Methyl and Ethyl Esters of Semicarbazinodiacetic Acid.—A semicarbazide solution is prepared according to the method of Bouveault and Locquin[4] in the following way: "130 g. (1 mol) hydrazine sulfate are dissolved in 500 cc. of boiling water, and to the hot solution 69 g. (0.5 mol) of potassium carbonate added in small portions. After allowing the solution to cool, 81 g. of potassium cyanate (1 mol) are added in several portions with the precaution of not allowing the temperature to rise. After this solution has stood 12 to 15 hrs., the potassium sulfate is precipitated in great part by the addition of 300 cc. of absolute alcohol and filtered off." This solution is assumed to contain 80% of the theoretical yield of semicarbazide. A concentrated aqueous solution of 227 g. of monochloroacetic acid (3 mols) is next prepared and neutralized with 165.5 g. of potassium carbonate (1.5 mols). The semicarbazide solution is now mixed with the potassium chloroacetate solution, and, after the reaction has proceeded in a boiling water bath for 12 hrs., the solution is evaporated to dryness *in vacuo*. For esterification, it is best to crush the flask and cut the sticky salt cake into small bits. Prepared in this way, the salt cake, on boiling with alcohol, disintegrates into a form suitable for the action of alcoholic HCl, and after this preliminary treatment, is allowed to stand with 300 cc. of 8% alcoholic acid for one week. At the end of this time, to the alcoholic solution of the ester filtered from inorganic salts, there is added a slight excess of ammonia, the alcohol is then distilled off *in vacuo*, the residue taken up in water, and the ester extracted with chloroform. A small amount of ester may be obtained by re-esterification of the salt residue obtained from the mother liquor left after extracting the ester as above with chloroform. 130 g. of hydrazine sulfate

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[1] Cf. *Ber.*, **33**, 1520 (1912).

[2] *Loc. cit.*

[3] THIS JOURNAL, **29**, 881 (1907).

[4] *Bull. soc. chim.*, **33**, 162 (1903).

worked up in the above way gave 34.9 g. of the methyl ester, and a second experiment to determine the yield of ethyl ester resulted in 39.3 g. of the latter substance. Figured on the basis of the hydrazine sulfate employed, the yield in either case is approximately 16%.

Methyl Semicarbazinodiacetate, $NH_2CONHN(CH_2COOCH_3)_2$.—This ester can be purified by crystallization from alcohol or water. From alcohol it separates in long needles, which melt undecomposed at 143.5°. It is readily soluble in chloroform and water, more difficultly soluble in benzene, and only slightly soluble in ether.

Calc. for $C_7H_{13}O_5N_3$: C, 38.36; H, 5.93; N, 19.18. Found: C, 38.10; H, 6.06; N, 18.97.

Ethyl Semicarbazinodiacetate, $NH_2CONHN(CH_2COOC_2H_5)_2$.—The ethyl ester is more readily soluble than the methyl ester in all solvents. It is best purified by crystallization from ether, from which it separates slowly in a fine, granular, crystalline state. From benzene it is obtained in the form of thin plates with dome shaped end faces, as seen under the microscope, and melts to a clear liquid at 91°.

Calc. for $C_9H_{17}O_5N_3$: C, 43.72; H, 6.88; N, 17.00. Found: C, 43.52, 43.70; H, 7.05, 6.93; N, 16.79, 17.15.

Semicarbazinodiacetohydrazide, $NH_2CONHN(CH_2CONHNH_2)_2$.—Hydrazine hydrate (2 mols) and methyl semicarbazinodiacetate (1 mol) mixed in concentrated aqueous solution react readily at water bath temperature. The hydrazide, which separates out, can be purified by precipitation from a concentrated solution in water with alcohol. It melts at 149°, decomposing on heating a few degrees higher.

Calc. for $C_5H_{13}O_3N_7$: C, 27.40; H, 5.94; N, 44.75. Found: C, 27.23; H, 6.05; N, 44.85.

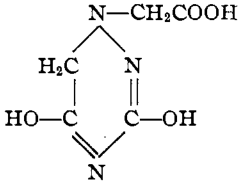
Dibenzal-semicarbazinodiacetohydrazide, $NH_2CONHN(CH_2CONHN = CHC_6H_5)_2$.—On agitating an aqueous solution of the hydrazide with benzaldehyde, the benzal compound quickly precipitates in quantitative yield. Purified by crystallization form alcohol, it melted at 178° with gas evolution.

Calc. for $C_{19}H_{21}O_3N_7$: N, 24.81. Found: N, 24.85.

Action of Nitrous Acid on Methyl Semicarbazinodiacetate.—When equimolecular amounts of methyl semicarbazinodiacetate, sodium nitrite, and hydrochloric acid are brought together in water as a solvent, the solution immediately assumes a deep yellow color and simultaneously a slow, steady gas evolution begins. The gas has the characteristic odor of nitrous oxide, and is mixed with carbon dioxide. After several hours' standing, the gas evolution stops and the original yellow color of the solution is almost completely discharged. The methyliminodiacetate formed can be removed by extraction with ether, from which it precipitates as a hydrochloride, on leading into the ether hydrochloric acid gas. This substance is described by Jongkees.[1] He gives the decomposition point as 183°, which agrees with our observation, when the substance is rapidly heated.

Calc. for $C_6H_{11}O_4N.HCl$: N, 7.09; HCl, 18.48. Found: N, 7.38; HCl, 18.73.

Esters of 3,5-Dioxy-1,6-dihydro-1,2,4-triazine-1-acetic Acid,



Ethyl Ester.—When treated with one mol of sodium ethoxide in ethyl alcohol solution, ethyl semicarbazinodiacetate loses a molecule of alcohol passing to the sodium salt of the ester of the above triazine acid. The same substance is obtained when methyl semicarbazinodiacetate is treated with sodium ethoxide in ethyl alcohol solution. If, on the other hand, the ethyl ester of the semicarbazino acid is treated with sodium methoxide in methyl alcohol solution, a salt of the methyl ester of the triazin acid results. In the preparation of the ethyl ester, a solution of sodium ethoxide, from 0.7 g. metallic sodium and 5 cc. of ethyl alcohol, was added to 5 g. of methyl semicarbazinodiacetate in 25 cc. of ethyl alcohol. A sodium salt of the triazine ester separated out, but this was not filtered off. After 5 hrs. 35 cc. *N* HCl was added, the slight excess of HCl neutralized with ammonia, the solution evaporated to dryness, the residue taken up with a little water, and the triazine extracted with chloroform. This product proved identical with the triazine prepared by substituting the ethyl ester of semicarbazinodiacetic acid for the methyl ester in the above experiment. The new substance can be crystallized from water, alcohol, or acetic ether, in all of which solvents it is readily soluble. It is more difficultly soluble in benzene, and very sparingly soluble in ether. From alcohol it crystallizes in radiating bunches of short slender needles, which melt undecomposed at 138.5°.

Calc. for $C_7H_{11}O_4N_3$: C, 41.79; H, 5.47; N, 20.90. Found: C, 41.59, 41.55; H, 5.45, 5.57; N, 20.84.

Methyl Ester.—The triazine methyl ester was prepared similarly to the ethyl ester from both methyl and ethyl semicarbazinodiacetate. The yield of ester obtained here was about 70% of the theoretical. This ester is much more difficultly soluble in water than is the corresponding ethyl ester, so that it separates out in great part, when, in its preparation, the sodium salt of the triazine ester is neutralized with HCl. The methyl ester is readily soluble in hot water, less soluble in alcohol, difficultly

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[1] *Rec. trav. chim.*, **27**, 287 (1908).

soluble in chloroform and acetic ether, and insoluble in ether. From water, the methyl ester crystallizes in characteristic short, thick prisms with dome shaped end faces, melting undecomposed at 183.5°.

Calc. for $C_6H_9O_4N_3$: C, 38.50; H, 4.81; N, 22.46. Found: C, 38.33; H, 4.93; N, 22.77.

Semicarbazinodiacetic Acid, $NH_2CONHN(CH_2COOH)_2$.—The esters of semicarbazinodiacetic acid are readily saponified by boiling with the calculated amount of potassium hydroxide solution. For the isolation of the semicarbazinodiacetic acid, the potassium salt, as thus prepared, is treated with the requisite quantity of hydrochloric acid, the solution evaporated to dryness, and the residue extracted with alcohol. The acid precipitates from the alcohol in a fine granular condition on the addition of ether. It can also be obtained as a barium salt directly from the reaction product of potassium monochloroacetate on semicarbazide by neutralizing the reaction mixture with barium hydroxide, whereupon the difficultly soluble barium salt separates out. From this salt, the semicarbazino acid can be obtained in the usual way by removing the barium as sulfate. The acid may be recrystallized from either alcohol or water in long rectangular plates, which on heating decompose with gas evolution at 161°. It has a very acid taste. The barium, calcium and zinc salts are difficultly soluble in water. Treated with sodium nitrite, an aqueous solution of the acid assumes a deep yellow color, but the nitroso compound here formed immediately begins to decompose with gas evolution. The acid titrates dibasic.

Calc. for $C_5H_9O_5N_3$: C, 31.41; H, 4.71; N, 21.99. Found: C, 31.15; H, 4.77; N, 22.25

Calcium Semicarbazinodiacetate, $C_5H_7O_5N_3Ca.4.5H_2O$.—For the preparation of the salts of semicarbazinodiacetic acid, a solution of the potassium salt was made, which with soluble salts of calcium, barium and zinc shows a precipitation. These salts are all difficultly soluble in water, and were not recrystallized for analysis. The calcium salt separates slowly from solution in the form of short, thick prisms. For the complete dehydration of the salt, we employed a temperature of 180°.

Calc. for $C_5H_7O_5N_3Ca.4H_2O$: Ca, 12.90; H_2O, 26.13. Found: Ca, 12.70, 12.69; H_2O, 26.54.

Barium Semicarbazinodiacetate, $C_5H_7O_5N_3Ba.H_2O$.—The barium salt, prepared by adding barium chloride to a solution of potassium semicarbazinodiacetate, shows no definite crystalline form under the microscope. Our analysis indicates the presence of a molecule of water of crystallization, but the salt showed no loss in weight on heating as high as 180°.

Calc. for $C_5H_7O_5N_3Ba.H_2O$: Ba, 39.89; N, 12.21. Found: Ba, 39.52, 39.82; N, 12.35.

Zinc Semicarbazinodiacetate, $C_5H_7O_5N_3Zn.H_2O$.—The zinc salt, made by the method employed for the calcium and barium salts, was obtained in the form of thin plates with dome-shaped end faces, as seen under the microscope. The zinc determination on a sample of the salt dried at 100° indicates a molecule of water of crystallization.

Calc. for $C_5H_7O_5N_3Zn.H_2O$: Zn, 24.01. Found: Zn, 24.15.

Preparation of Hydrazinodiacetic Acid, $NH_2N(CH_2COOH)_2$, *from Methyl Semicarbazinodiacetate.*—As hydrazinodiacetic acid is decomposed by acids similar to nitrilotriacetic acid, it was attempted to split off the urea rest from the semicarbazino ester with alkali. In this experiment the conditions followed were to heat the semicarbazino ester with 3 mols of 3*N* KOH in a sealed tube at 150° for two hrs. At the end of this time the ammonia was distilled off and 3 mols of standardized HCl added. On concentration of the solution to a point just sufficient to hold the inorganic salts in solution, the hydrazinodiacetic acid crystallized out in a yield of about 75% to 80% of the theoretical. In one experiment the yield of hydrazinodiacetic acid obtained was 77% of the theoretical, and a titration of the ammonia liberated in the reaction indicated a decomposition of 75.76%. There is necessarily a slight loss of ammonia in the transfer from the pressure tube to the distilling flask, and a further slight discrepancy in the results may be accounted for by a small amount of potassium chloride in the hydrazine acid as weighed. On evaporation of the filtrate from the hydrazine acid and esterification of the residue with 8% ethyl alcoholic HCl in the cold, about 15% of the original semicarbazino ester may be regained.

Hydrazinodiacetic acid can also be prepared by the action of KOH at 150° on the barium salt of semicarbazinodiacetic acid, as obtained above directly from the reaction product of potassium chloroacetate on semicarbazide, but the yield obtained by this method was not satisfactory.

Preparation of Hydrazinodiacetic Acid from Potassium Chloroacetate and Hydrazine Hydrate.[1]—The following modification of the method of Curtius and Hussong is to be recommended in the preparation of hydrazinodiacetic acid. Neutralize 80 g. of monochloroacetic acid (2 mols) in 200 cc. of water by adding in small portions 58 g. of potassium carbonate (1 mol) and then pour into this solution of potassium chloroacetate 21 g. of hydrazine hydrate (1 mol). A second 58 g. of potassium carbonate are now added gradually, whereupon, with a steady evolution of CO_2, the temperature rises to about 70°. The solution is now heated as long as gas evolution continues. At the end of the reaction, the hydrazinodiacetic acid is precipitated by making the solution acid to Congo paper with hydrochloric acid.[2]

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[1] *J. prakt. Chem.*, [2] **83**, 271 (1861).

[2] The following conditions were established as suitable for the preparation of hydrazinomonoacetic acid from potassium chloroacetate and hydrazine hydrate: Into 42 g. of 50% hydrazine hydrate (Kahlbaum), allow to drop rapidly with constant stirring, a solution of potassium chloroacetate, prepared from 21 g. of potassium car-

The hydrazine acid thus obtained is freed from any admixed potassium chloride by recrystallization from water. The hydrazinodiacetic acid, obtained by the action of potassium hydroxide on the methyl ester of semicarbazinodiacetic acid, proved identical with the above preparation from hydrazine hydrate. Curtius and Hussong state that the hydrazine acid, on heating, melts with violent gas evolution at 166°–167°. Our observation is that the substance begins to take on a yellow color at 165° and decomposes suddenly and completely at 176°. Despite the fact that the substance contains two carboxyls it has not an acid taste. Its solubility in water is 1:108 at 22° and 1:46 at 100°. The following analysis was made on a sample obtained from the ester of semicarbazinodiacetic acid.

Calc. for $C_4H_8O_4N_2$: C, 32.43; H, 5.41; N, 18.92. Found: C, 32.26; H, 5.53; N, 18.86.

Barium Hydrazinodiacetate, $C_4H_6O_4N_2Ba.H_2O$.—The barium salt of hydrazinodiacetic acid was made by adding the calculated amount of barium chloride to a solution of the acid, neutralized with potassium hydroxide. The barium salt separates out slowly in a finely divided state, showing no definite crystalline form. Heated to 150°, it loses one molecule of water.

Calc. for $C_4H_6O_4N_2Ba.H_2O$: Ba, 45.58; H_2O, 5.98. Found: Ba, 44.74; H_2O, 6.53.

Zinc Hydrazinodiacetate, $C_4H_6O_4N_2Zn$.—The zinc salt was prepared similarly to the barium salt and resembles it very closely in its physical properties. Neither the barium nor zinc salt could be purified by recrystallization.

Calc. for $C_4H_6O_4N_2Zn$: Zn, 31.03. Found: Zn, 30.81.

Esters of Hydrazinodiacetic Acid.—Curtius and Hussong prepared the ethyl ester of hydrazinodiacetic acid from the silver salt of the acid and

bonate and 29 g. of monochloroacetic acid (1 mol.). At the same time add, in small quantities, a second batch of 21 g. of potassium carbonate to the hydrazine solution, timing the process so as to bring it to a close with the addition of the potassium chloroacetate. To insure completion of the reaction, next heat the solution to boiling one-half hour. In this reaction there is formed both the hydrazinomono- and di-acetic acid. The latter separates on making the solution acid with hydrochloric acid. For the isolation of the hydrazinomonoacetic acid, the solution, filtered from the hydrazinodiacetic acid, is evaporated to dryness, 150 cc. of alcohol poured on the salt cake, and finally hydrochloric acid gas led in to saturation. The esterification is then allowed to proceed in the cold twelve hours, when the solution is heated to boiling and filtered hot from the salt residue. On cooling, the hydrochloride of the hydrazino ester crystallizes out. The yields, in the one experiment tried, were 16 g. of hydrazinodiacetic acid and 7.3 g. of the hydrochloride of hydrazinomonoacetic acid ethyl ester. Darapsky and Prabhaker[4] obtained from 20 g. of hydrazine hydrate (equal to 40 g. of 50% hydrate used above) 6.4 g. of the hydrochloride of the ester of hydrazinoacetic acid, using a method similar to that of Curtius and Hussong for preparing hydrazinodiacetic acid.—J. R. BAILEY and L. A. MIKESKA, *Ber.*, 45, 1660 (1912).

ethyl iodide, and found it to be a "syrup," which they were unable to crystallize. The same substance was obtained by esterification with alcoholic HCl. We repeated their last experiment and obtained the hydrochloride of the ethyl ester as a viscous oil, readily soluble in alcohol, but which we were unable to crystallize. On dissolving in a concentrated aqueous solution of this salt an equimolecular amount of potassium cyanate, ethyl semicarbazinodiacetate crystallized out after stirring a few minutes, and proved identical with the esterification product of the acid already described, obtained by the interaction of potassium chloroacetate and semicarbazide. A nitrogen determination was made on the semicarbazino ester made by this second process.

Calc. for $C_9H_{17}O_5N_3$: N, 17.00. Found: N, 17.30.

Hydrazinodiacetic acid is insoluble in both ethyl and methyl alcohol, but quickly dissolves in either with rapid esterification on leading hydrochloric acid gas into a suspension of the acid in alcohol. We found that the methyl ester gives a beautifully crystallizing hydrochloride. For analysis it was crystallized from methyl alcohol in slender microscopic needles, which melted with gas evolution at 174.5°.

Calc. for $C_6H_{12}O_4N_2.HCl$: N, 13.13; HCl, 17.18. Found: N, 13.33; HCl, 17.10.

This salt was likewise converted to the semicarbazino ester by the action of potassium cyanate, and the substance thus obtained proved identical with the esterification product of CH_3OH-HCl on semicarbazinodiacetic acid. As a further confirmation, a nitrogen determination was made.

Calc. for $C_7H_{13}O_5N_3$: N, 91.18. Found: N, 19.41.

Phenylthioureidaminodiacetic Acid Methyl Ester, $C_6H_5NHCSNHN(CH_2COOCH_3)_2$.—The above substance was prepared by dissolving the hydrochloride of hydrazinodiacetic acid methyl ester and sodium bicarbonate in equimolecular amounts in a little water, adding one mol of phenyl mustard oil dissolved in alcohol, and heating this mixture one hour to boiling. The alcohol was then distilled off and the mustard oil compound crystallized from alcohol, from which it separated in long needles, melting undecomposed at 120°. This compound is readily soluble in the common solvents with the exception of ether, petrolic ether, and water.

Calc. for $C_{13}H_{16}O_4N_3S$: N, 13.55. Found: N, 13.56.

Action of Formaldehyde on Hydrazinodiacetic Acid.—All attempts of Curtius and Hussong to condense hydrazinodiacetic acid with aldehydes were without result. We repeated some of their experiments in this direction and were likewise unable to bring about a reaction. However, formaldehyde reacts in a peculiar way with this hydrazine. If hydrazinodiacetic acid be covered with ordinary formalin, the hydrazine after a short time dissolves, forming a yellow solution, which becomes red on standing. If the hydrazine be warmed with the formaldehyde solution, it immediately dissolves with a violent evolution of carbon dioxide, and the reaction product can be precipitated by the addition of alcohol as a crystalline, slightly yellow substance, which was not further investigated.

Conversion of Hydrazinodiacetic Acid to Iminodiacetic Acid by the Action of Sodium Nitrite.—To 2 g. of the hydrazine acid covered with 15 cc. of water were added 1 g. of sodium nitrite and 5 cc. of water. The hydrazine dissolved after a few minutes stirring, with an evolution of a colorless gas, probably N_2O. At the end of the reaction, the calculated amount of standard hydrochloric acid was added to liberate the iminodiacetic acid, and the solution was then concentrated to a small volume. After standing over night, 1.2 g. of the characteristic crystals of iminodiacetic acid separated out. This product proved identical with a sample made according to the method of Heintz.[1] Eschweiler found that this substance melts with decomposition at about 225°,[2] while Johnson gives the decomposition point at 235–236°.[3] Our determination agreed with that of Johnson.

Calc. for $C_4H_7O_4N$: C, 36.09; H, 5.26; N, 10.53. Found: C, 36.06; H, 5.36; N, 10.66.

Action of Sulfuric Acid on Hydrazinodiacetic Acid.—In one experiment 0.5 g. of hydrazinodiacetic acid was heated in a sealed tube with 10 cc. of 2.85 N H_2SO_4 2 hrs. at 150°. The solution was then made alkaline with a slight excess of barium hydroxide and the liberated ammonia estimated. Calculated for 1 mol of ammonia, 3.38 cc. N acid; used, 3.65 cc. This result agrees with a similar determination made by Curtius and Hussong in their study of the action of acids on hydrazinodiacetic acid. After exact removal of the barium as sulfate, the solution from the ammonia distillation was evaporated to dryness and the residue purified to some extent by dissolving in water and precipitating with alcohol. A substance was thus obtained which, on heating, began to show signs of decomposition at about 200°, contracted on further heating, and decomposed completely between 225° and 230° (uncor.). This observation agrees quite well with the behavior of glycocoll on heating. In order to confirm fully the formation of glycocoll in the above decomposition of hydrazinodiacetic acid, the experiment was repeated though with slight modification. In this second experiment 5 g. of hydrazinodiacetic acid and 20 cc. of 7.7 normal sulfuric acid were heated two hours at 150°. There was considerable pressure on opening the tube, and after standing three days, 0.5 g. of a crystalline substance had separated out. This proved to be Heintz's "Triglycolamidsäure," $N(CH_2COOH)_3$.[4] It was compared with a sample of nitrilotriacetic acid, made according to

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[1] *Ann.*, **122**, 257 (1862).

[2] *Ibid.*, **278**, 231 (1894).

[3] *Am. Chem. J.*, **35**, 65 (1907).

[4] *Ann.*, **122**, 269 (1862).

the method of Heintz, and in addition a nitrogen determination was made. According to our observation, nitrilotriacetic acid decomposes at 246° to a reddish brown liquid. Polstorff and Meyer[1] give 239° as the decomposition point (probably uncor.).

Calc. for $C_6H_9O_6N$: N, 7.33. Found: N, 7.69.

The acid filtrate from the nitrilotriacetic acid was heated with an excess of barium carbonate, and after removal of the barium salts the dissolved barium was precipitated as sulfate. The residue obtained by evaporating the filtered solution was taken up with water, and after neutralization with the calculated amount of potassium hydroxide, shaken with a slight excess of phenylisocyanate, according to the method of Paal.[2] A small amount of diphenyl urea was filtered off, and the solution made acid with hydrochloric acid. 1.5 g. of phenylureidoacetic acid crystallized out. This was compared with a preparation made according to the method of Paal. On heating with concentrated hydrochloric acid, this hydantoic acid showed the behavior of phenylhydantoic acid, as recorded by Mouneyrat,[3] in that it was converted to 2-phenylhydantoin, melting at 159 to 160°. A nitrogen determination, made on the phenylureidoacetic acid, gave the following result:

Calc. for $C_9H_{10}O_3N_2$: N, 14.43. Found: N, 14.75.

Oxidation of the Esters of Semicarbazinodiacetic Acid. Ethyl Ester of Glyoxylic Acid Semicarbazone, $NH_2CONHN = CHCOOC_2H_5$.—When to a concentrated aqueous solution of the ethyl ester of semicarbazinodiacetic acid, made acid with sulfuric acid, a concentrated solution of potassium permanganate is added, oxidation proceeds for some time without gas evolution, and after a while a difficultly soluble substance separates, which proved to be the semicarbazone of glyoxylic acid ethyl ester. The yield is poor and we did not attempt to isolate any other products of the reaction. It is possible that ethyl glycolate is formed as an intermediary product, but according to Schreiner[4] this ester would immediately be saponified by water into the corresponding acid. Although the oxidation proceeds for some time without gas evolution, the primary oxidation products later decompose on further addition of permanganate with gas evolution. The ethyl ester of glyoxylic acid semicarbazone was also preprepared by oxidizing with permanganate Traube's ethyl semicarbazinoacetate,[5] the reaction proceeding here similarly to the oxidation of ethyl semicarbazinopropionate.[6] The structure of the ester of glyoxylic acid

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[1] *Ber.*, **45**, 1910 (1912).
[2] *Ibid.*, **27**, 975 (1894).
[3] *Ibid.*, **33**, 2394 (1900).
[4] *Ann.*, **197**, 7 (1879).
[5] *Ber.*, **31**, 166 (1898).
[6] *Ann.*, **303**, 83 (1898).

semicarbazone was further confirmed by esterifying with alcoholic hydrochloric acid glyoxylic acid semicarbazone, which had been prepared from chloral hydrate and semicarbazide. A substance of the formula $NH_2CONHN = CHCOOC_2H_5$ is described by Simon and Chavanne,[1] but the properties of their semicarbazone do not agree with those, as determined by us, for the oxidation product of ethyl semicarbazinodiacetate. They describe their product as follows: "It melts with decomposition at 228°, is apparently insoluble in almost all solvents, but is readily soluble in boiling water with partial saponification." We find that the substance, when slowly heated, melts with gas evolution to a brown liquid at 211°, but on rapid heating, the decomposition takes place at about 218°. Our preparation was purified by crystallization from water and alcohol. In recrystallizing from water, it did not show any tendency to saponify. The substance crystallized from alcohol has the form of long, slender prisms, the faces of which have the appearance of being etched.

Calc. for $C_5H_9O_3N_3$: C, 37.71; H, 5.63; N, 26.42. Found: C, 37.57; H, 5.63; N, 26.60.

The above ester was prepared as follows from glyoxylic acid semicarbazone, obtained by the action of chloral hydrate on semicarbazide:[2] 3 g. of the semicarbazone acid were suspended in 150 cc. of 8% alcoholic hydrochloric acid and the solution heated to boiling 45 min. The alcohol was then distilled off, the residue taken up with a little water and made slightly alkaline with ammonia. The semicarbazone ester prepared in this way has a slight yellow color, which is completely removed by recrystallization from water with the addition of animal charcoal.

Oxidation of Methyl Semicarbazinodiacetate with Bromine.—Only a very small yield of the semicarbazone methyl ester was obtained by oxidizing the semicarbazino methyl ester with potassium permanganate. The esterification was therefore carried out with bromine under the following conditions: 5 g. of the semicarbazino methyl ester were dissolved in 40 cc. of water and 1.5 cc. of bromine (1.2 cc. corresponds to one mol) aspirated into this solution. The bromine was instantaneously reduced and 0.75 g. of the oxidation product separated out, corresponding to 22.7% of the theoretical yield of semicarbazone. This semicarbazone is readily soluble in hot water, and more difficultly soluble in alcohol. It crystallizes from water in a fine, granular condition. If it is heated and the bath kept at 206° for a few minutes it melts completely at this temperature with decomposition.

Calc. for $C_4H_7O_3N_3$: C, 33.10; H, 4.83; N, 28.97. Found: C, 33.27; H, 4.97; N, 29.31.

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[1] *Compt. rend.*, **143**, 904 (1906).

[2] *Ber.*, **45**, 2624 (1912).

Preparation of Ethyl Semicarbazinoacetate, $NH_2CONHNHCH_2COOC_2H_5$, *from Semicarbazide and Monochloroacetic Acid.*—In the action of potassium chloroacetate on semicarbazide, there is always formed both semicarbazinomono- and di-acetic acid. In the preparation of the former substance, it is best to use only one-third of the potassium chloroacetate recommended above in the preparation of the diacetic derivative. Esterification of the semicarbazinoacetic acid is best effected with boiling 3% alcoholic HCl, from which the HCl salt of the ester crystallizes on cooling. The yield of semicarbazinoacetic acid ethyl ester, obtained by this method, was only 3 g. from 40 g. of semicarbazide. Purified by recrystallization from alcohol, the ester melted at 122°, as reported by Traube,[1] and proved identical with the ester obtained below by reducing glyoxylic acid semicarbazone and esterifying the reduction product.

Calc. for $C_5H_{11}O_3N_3$: C, 37.27; H, 6.83; N, 26.08. Found: C, 37.32; H, 6.96; N, 26.33.

Preparation of Ethyl Semicarbazinoacetate by Esterification of the Reduction Product of Glyoxylic Acid Semicarbazone.—11.8 g. of glyoxylic acid semicarbazone were reduced with sodium amalgam, according to the directions of Darapsky and Prabhaker,[1] after neutralization of the reduction liquid with hydrochloric acid, the solution was evaporated to dryness, and the residue esterified by boiling with 250 cc. of 3% alcoholic hydrochloric acid for one hour. The alcohol solution was filtered hot from the insoluble inorganic salts. On cooling, 9.2 g. of the hydrochloride of the ethyl ester of semicarbazinoacetic acid crystallized out. The filtrate from the hydrochloride of the ester was put back on the salt mass and boiled another hour. The alcohol was then filtered off, the HCl neutralized with ammonia, the boiling solution filtered from the ammonium chloride, and the filtrate evaporated to dryness. The residue, on extraction with alcohol, yielded 4 g. of crude semicarbazino ester, which gave 2.1 g. pure substance on recrystallization. The total yield was about 66% of the theoretical. Darapsky and Prabhaker obtained a yield of 50.4% of the theoretical in working up the reduction product of glyoxylic acid semicarbazone to the HCl salt of the ethyl ester of hydrazinoacetic acid, $HCl.NH_2NHCH_2COOC_2H_5$. For analysis the hydrochloride of semicarbazinoacetic acid ethyl ester was recrystallized from alcohol. It decomposes at 170° with gas evolution.

Calc. for $C_5H_{11}O_3N_3.HCl$: N, 21.27; HCl, 18.50. Found: N, 21.42; HCl, 18.53.

Semicarbazinoacetic Acid, $NH_2CONHNHCH_2COOH$.—The ester of semicarbazinoacetic acid is readily saponified by digestion for one-half hour in aqueous solution with one-half mol of barium hydroxide. On allowing the reaction mixture to cool, the difficultly soluble barium salt crystallizes out, from which the acid can be liberated by exactly removing

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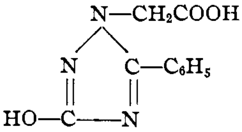
[1] *Loc. cit.*

the barium as sulfate and concentrating the solution to the point of crystallization. It is readily soluble in water and difficultly soluble in alcohol. The acid melts at 143°.

Calc. for $C_5H_7O_3N_3$: N, 31.58. Found: N, 31.86.

Benzoyl Derivative of Ethyl Semicarbazinoacetate, $NH_2CONHN(COC_6H_5)CH_2COOC_2H_5$.—Ethyl semicarbazinoacetate (1 mol) was heated in acetic ether solution for one hour with benzoyl chloride (1 mol), and to neutralize the hydrochloric acid liberated in the reaction, sodium bicarbonate (1 mol) was suspended in the acetic ether. The benzoyl derivative was isolated from the solution by concentrating this to a small volume and adding ether. It is readily soluble in water, alcohol and acetic ether, and difficultly soluble in ether and benzene. It crystallizes from water in rectangular plates, which melt undecomposed at 172°.

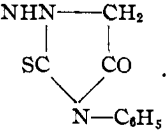
Calc. for $C_{12}H_{15}O_4N_3$: C, 54.34; H, 5.66; N, 15.85. Found: C, 54.02; H, 5.82; N, 15.91.

Conversion of the Benzoyl Derivative of Ethyl Semicarbazinoacetate to 3-Oxy-5-phenyltriazol-1-acetic Acid,  .—The above described benzoyl derivative was converted into a triazol by heating with 10% potassium hydroxide solution for one-half hour, and the triazol was then precipitated by acidifying with hydrochloric acid.[1] It is moderately soluble in both alcohol and water, and can best be purified by crystallization from glacial acetic acid. On slowly heating it decomposes to a red liquid at 256°, beginning to melt at 253°.

Calc. for $C_{10}H_9O_3N_3$: C, 54.79; H, 4.11; N, 19.18. Found: C, 54.44; H, 4.37; N, 18.94.

Ethyl 3-Oxy-5-phenyltriazol-1-acetate.—The triazol acid was esterified in the usual way by boiling with 6% alcoholic HCl for 3 hrs., the HCl was then neutralized with ammonia, the alcohol solution, filtered from the ammonium chloride, evaporated, and the residue taken up with water. On neutralizing the solution with ammonia, the ester separated out and was purified by crystallization from dilute alcohol. It melts undecomposed at 145°.

Calc. for $C_{12}H_{13}O_3N_3$: N, 17.00. Found: 17.30.

Action of Phenyl Mustard Oil on Ethyl Semicarbazinoacetate. 1-Ureido-3-phenyl-2-thiohydantoin,  .—Phenyl mustard oil and

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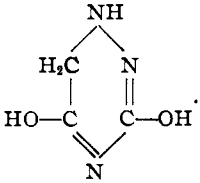
[1] Cf. *Ber.*, **29**, 1946 (1899); **33**, 1520 (1900); **45**, 30 (1912).

ethyl semicarbazinoacetate, in molecular proportions, were heated to boiling for one-half hour in glacial acetic acid solution. On cooling, the hydantoin crystallized out and was purified by recrystallizing from acetic acid and water. It is readily soluble in hot glacial acetic acid, and more difficultly soluble in alcohol and water. From the latter solvent it separates in thin plates with a pearly luster, which, on slow heating, melt with decomposition to a red liquid at 211°.

Calc. for $C_{10}H_{10}O_2N_4S$: C, 48.00; H, 4.00; N, 22.40; S, 12.80. Found: C, 47.53; H, 4.18; N, 22.61; S, 12.84.

Nitroso Derivative of Ethyl Semicarbazinoacetate, $NH_2CONHN(NO)CH_2COOC_2H_5$.—The hydrochloride of ethyl semicarbazinoacetate and sodium nitrite in aqueous solution readily react to form a stable nitroso compound. This separates out, when the solution is concentrated, or can be extracted with ether or chloroform. The nitroso compound is soluble in the common solvents with the exception of petrolic ether, and can be purified by recrystallizing from benzene. It is of a light yellow color and gives the Liebermann reaction. Heated with 10% KOH, the nitroso compound decomposes with gas evolution. The substance begins to melt at 99° and decomposes completely at 102°.

Calc. for $C_5H_{10}O_4N_4$: C, 31.58; H, 5.26; N, 29.47. Found: C, 31.67; H, 5.25; N, 29.79.

3,5-Dioxy-1,6-dihydro-1,2,4-triazine,  . *Sodium Salt.*—When one mol of sodium ethoxide in alcohol is added to an alcoholic solution of ethyl semicarbazinoacetate, there results an immediate precipitation of the above triazine salt. For analysis the salt was boiled with absolute alcohol and washed with ether.

Calc. for $C_3H_4O_2N_3Na$: N, 30.65; Na, 16.79. Found: N, 30.44; Na, 17.05.

The free triazine may be prepared as follows, without isolating the sodium salt: After mixing the semicarbazino ester and sodium alcoholate in equimolecular amounts in alcohol, the calculated amount of standard HCl is added, the solution heated to boiling, and filtered. In this process only a small amount of the triazine passes into the alcohol. The triazine is next separated from admixed sodium chloride by carefully leaching out the salt with the least possible quantity of cold water. It can be purified best by recrystallization from water, in which it is readily soluble, and from which it crystallizes in prismatic plates of a pearly luster, melting undecomposed at 221°. It is very difficultly soluble in alcohol, and insoluble in the other common organic solvents. A solution of the triazine decolorizes bromine water instantaneously.

Calc. for $C_3H_5O_2N_3$: N, 36.52. Found: N, 36.49.

Preparation of Ethyl Semicarbazinopropionate, $NH_2CONHNHCH(CH_3)COOC_2H_5$ *from Pyruvic Acid Semicarbazone*, $NH_2CONHN = CH(CH_3)COOH$.—The pyruvic acid semicarbazone[1] used in this experiment was made in a yield of about 92% by allowing semicarbazide and potassium pyruvate to react in aqueous solution. The reaction proceeds with a considerable generation of heat, and at its close the semicarbazone can be precipitated by adding the calculated amount of hydrochloric acid. The reduction was carried out just as in the case of glyoxylic acid semicarbazone, according to the method of Darapsky and Prabhaker, and the esterification process used there was found available in this preparation. The ethyl semicarbazinopropionate does not separate out as the hydrochloride, but is readily extracted from neutral solution with chloroform. Only one trial was made in the working out of the above process for the preparation of ethyl semicarbazinopropionate, and this resulted in a yield of 46% of the theoretical. In another experiment, the ethyl ester of pyruvic acid semicarbazone was reduced in boiling 80% alcohol with 5% sodium amalgam, according to the method of Kessler and Rupe,[2] and the reduction product isolated in the form of the ethyl ester as above. This experiment gave a yield of 64% of the theoretical. However, a further study of these reduction processes would be necessary in deciding the best method of making this semicarbazino ester. There is no doubt that semicarbazinopropionic acid esters can be more conveniently prepared from pyruvic acid semicarbazone than by the original method of Thiele and Bailey. The semicarbazinopropionic acid ethyl ester made as above was compared with a preparation made by the method of Thiele and Bailey, and the two samples were in every way identical. Further, the reaction products with benzyl chloride, phenyl mustard oil, and sodium alcoholate referred to in other parts of this article were made and found to agree with the description of these substances. A nitrogen determination on ethyl semicarbazinopropionate, prepared by the new process, follows.

Calc. for $C_6H_{13}O_3N_3$: N, 24.00. Found: N, 24.12.

Nitroso Derivative of Ethyl Semicarbazinopropionate, $NH_2CONHN(NO)CH(CH_3)COOC_2H_5$.—This nitroso compound was made similarly to the nitrososemicarbazinoacetic acid ethyl ester described above, and gives the Liebermann reaction. It crystallizes from acetic ether in long, slender prisms of a light yellow color, is readily soluble in water and

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[1] *Ann.*, 303, 87 (1898).

[2] *Loc. cit.*

alcohol, and difficultly soluble in ether and benzene. It melts with gas evolution at 134.5°.

Calc. for $C_6H_{12}O_4N_4$: C, 35.29; H, 5.88; N, 27.45. Found: C, 35.51; H, 5.97; N, 27.31.

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THE PREPARATION OF ACROLEIN.

BY EDGAR J. WITZEMANN.

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Although numerous methods have been proposed for the preparation of acrolein, it has remained relatively difficult to obtain it pure and in large quantities. The most practical method for obtaining pure acrolein hitherto has been the phosphoric acid method proposed by Nef,[1] used by McLeod,[2] and investigated in some detail by Bergh.[3] More recently Wohl and Mylo[4] have described a method for preparing acrolein in which anhydrous magnesium sulfate was used as the catalyst. However, the apparatus used by Wohl and Mylo is composed entirely of especially constructed parts so that the method, as described by them, cannot be used except after a large outlay in time and money for the construction of the apparatus. The present note is an account of a much simpler way of using magnesium sulfate in an apparatus composed of ordinary stock materials. The results obtained by this modification are not so good as the best results obtained by Wohl and Mylo, but the method, as described here, is much more available for ordinary use.

Before discussing the modification of Wohl and Mylo's method I wish to record my experience with the phosphoric acid method. The apparatus used was essentially like that used by Bergh. A three liter Kavalier round-bottom flask standing in a Babo funnel and heated by a ring burner was used instead of the iron retort employed by Bergh. That is, the apparatus was like that in Fig. 1, except that there was no dropping funnel in the generator flask and that the thermometer was pushed down into the glycerol.

Using an apparatus arranged in this way, a charge of 500 g., consisting of 475 g. of commercial glycerol and 25 g. of a pure phosphoric acid (d. 1.7), regularly gave 40–45 (sometimes 50 g.) of very pure acrolein. It is necessary to regulate the flame of the ring burner carefully because more

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[1] *Ann.*, **335**, 221 (1904).

[2] *Am. Chem. J.*, **37**, 35 (1907).

[3] *J. prakt. Chem.*, [2] **79**, 351 (1909).

[4] *Ber.*, **45**, 2050 (1912).