complete disintegration of the walls of the starch granules, as by excessive heat in the roasting process of dextrin manufacture. Its iodide in such a solution is not decolorized by toluene, whereas that of erythrodextrin is readily decolorized by that solvent.

7. In a number of cases long, colorless needles were obtained, probably as a decomposition product of the small amount of cellulose the starch contains. The best crystals were obtained as white needles by adding raw corn starch to boiling 0.011 *N* hydrochloric acid and boiling 150 minutes. At the end of this time the hydrolysis was somewhat more advanced than that represented by the final reading in Table VII, the amylodextrin having just entirely disappeared and the temperature of crystallization having fallen to 45°. At this time, however, these white crystals rather suddenly appeared, of less specific gravity than the (sphero-) crystals previously observed and forming at the constant temperature of 75°. This formation increased steadily in the next 1.5 hours, both crops of crystals being obtained.

8. Lintner's "soluble starch" is nearly pure amylodextrin, formed from the amylocellulose of potato starch and still held in the form of the original cells by a thin layer of insoluble material, which disintegrates in water at about 50°. The transition temperature of its iodide in 1% solution is 69.5°. It crystallizes with difficulty and only at low temperatures (below 50°) even from 10% solution, showing the important role of the higher polysaccharides in the ordinary crystallization of "artificial starch" (cf. Table VII).

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[CONTRIBUTIONS FROM THE SHEFFIELD CHEMICAL LABORATORY OF YALE UNIVERSITY.]

RESEARCHES ON THIOCYANATES AND ISOTHIOCYANATES.

XII. THE POLYKETIDE ISOTHIOCYANATE—ETHYL ISOTHIOCYANPROPIONATE.

BY TREAT B. JOHNSON AND ARTHUR A. TICKNOR.

Received January 2, 1918.

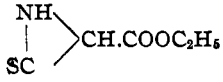
The first polyketide isothiocyanate (mustard oil) to be described in the literature, whose constitution has been definitely established, is ethyl isothiocyanacetate (I), which has been synthezised by Johnson and Hemingway.[1] This is obtained in good yield by the action of thiophosgene on ethyl aminoacetate or its hydrochloric acid salt, while its isomer (II) results by interaction of potassium thiocyanate with ethyl chloroacetate in alcohol solution. Both esters boil at practically the same temperature without appreciable decomposition, and it has been our experience that neither isomer exhibits any tendency to undergo molecular rearrangement

[1] THIS JOURNAL, 38, 1550 (1916).

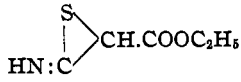
during distillation. Whether the isothiocyanate (II) can be rearranged into the isomeric modification (I) by heating at a higher temperature remains to be established.

$SCN.CH_2COOC_2H_5$ (I). $NCS.CH_2COOC_2H_5$ (II).

In the case of acetic acid only two rhodan derivatives or corresponding esters are to be taken into account, if we exclude from consideration the theoretically possible cyclic combinations represented by Formulas III and IV.

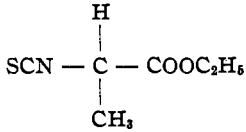


(III).

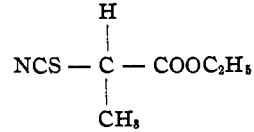


(IV).

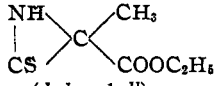
When one considers, on the other hand, the higher homologs of acetic acid a greater number of theoretical possibilities have to be taken into consideration due to the fact that in the α-rhodan derivatives of such acids, we are dealing with combinations containing an asymmetric carbon atom. For example, in the case of ethyl α-rhodanopropionate, we have to deal not only with the two structural thiocyanate isomers represented by Formulas V and VI, but also with the two active modifications of each of these two forms making a total of six isomers conforming to the formula $C_6H_9O_2NS$. Of these six modifications only one has been described in the literature, namely, *dl*-ethyl thiocyanopropionate which was synthesized by Wheeler and Barnes[1] by allowing ethyl α-bromopropionate to interact with potassium thiocyanate. If we take into consideration the theoretically possible cyclic combinations (VII) and VIII), and their respective active modifications then the total number of isomeric ethyl α-rhodonopropionates possible can be increased to twelve. These are represented by the following structural formulas:



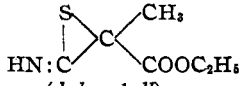
(*d*, *l* and *dl*)
(V).



(*d*, *l* and *dl*)
(VI).



(*d*, *l* and *dl*)
(VII).



(*d*, *l* and *dl*)
(VIII).

It is of interest to note here that both cyclic modifications of ethyl thiocyan- and isothiocyanacetate represented by Formulas III and IV, respectively, contain an asymmetric carbon atom. As far as the writer

[1] *Amer. Chem. J.*, **24**, 76 (1900).

is aware, there is no series of simple aliphatic compounds containing a single asymmetric carbon atom that presents so many possibilities of structural isomerism as these secondary rhodan combinations.

We have now made a further application of the thiophosgene synthesis of isothiocyanates and found that it is possible to convert the ethylester of alanine smoothly into its corresponding unknown isothiocyanate derivative represented by Formula V. The mustard oil is obtained in good yield by interaction of thiophosgene with the free aminoacid ester as well as with its hydrochloride. Not only have we prepared the racemic modification of this rhodanide, but we have also applied the reaction successfully with the ethyl ester of active alanine and synthesized the *dextro-* modification of the isothiocyanate. The alanine used in this latter work was an active preparation purchased from Kahlbaum and also material which was manufactured for our work by hydrolysis of silk fibroin. Both the *racemic* and *dextro* forms of the isothiocyanates are colorless oils when pure and boil at practically the same temperature, under diminished pressure, as the normal thiocyanate described by Wheeler and Barnes.[1] There is no apparent tendency to undergo rearrangement during distillation in either case.

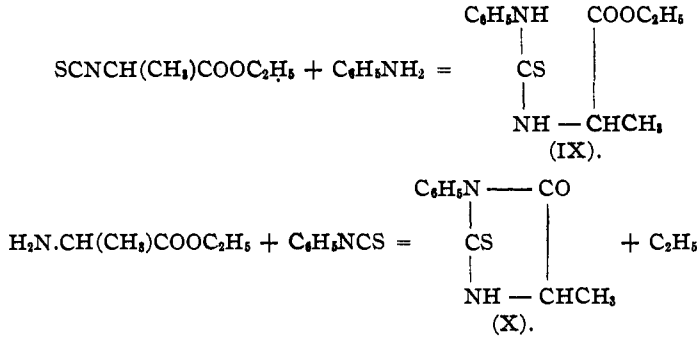
dl-NCS.CH(CH_3)$COOC_2H_5$.....	Boils at 107–108° at 16 mm.
dl-SCN.CH(CH_3)$COOC_2H_5$.....	Boils at 102–107° at 16–17 mm.
dl-SCN.CH(CH_3)$COOC_2H_5$.....	Boils at 106–108° at 16–17 mm.

As in the case of ethyl isothiocyanacetate the structure of its higher homolog—ethyl isothiocyanopropionate—is established by its behavior towards aniline. We have shown in our previous paper[2] that the isothiocyanacetate and aniline interact with formation of the thiohydantoate $C_{11}H_{14}O_2N_2S$. Fischer[3] applied the reverse reaction by combining phenyl mustard oil with ethyl aminoacetate and obtained the same acyclic derivative. We now find that an entirely different behavior is shown when applying similar reactions with our new isothiocyanate and alanine ester. Aniline and ethyl isothiocyanopropionate combined smoothly as in the case of the acetate combination to form the thiohydantoate represented by Formula IX. When we reversed the procedure and allowed phenyl mustard oil to combine with ethyl α-aminopropionate an entirely different result was obtained, although we apparently worked under practically identical experimental conditions. Here the hydantoate was apparently first formed, but the heat generated by combination was sufficient to cause an inner condensation with production of the cyclic combination 1-phenyl-2-thio-4-methylhydantoin with evolution of alcohol. The changes are represented below:

[1] *Loc. cit.*

[2] Johnson and Hemingway, *Ibid.*

[3] *Ber.*, **34**, 440 (1904).



(IX).

(X).

While inactive ethyl isothiocyanopropionate and aniline interacted to give a crystalline thiohydantoate, when the same reaction was applied with the active ester an oil was obtained which showed no tendency to crystallize. In fact a sample of the reaction product was preserved for six months without undergoing any apparent change.

A second reaction which characterized our rhodanide as an isothiocyanate was its behavior towards ethyl alcohol. The two compounds interact smoothly on heating with formation of the thionurethane. This

$$C_2H_5OOC.CH(CH_3).NH.CSOC_2H_5$$

is a representative of a new type of acyclic combinations and is a crystalline combination melting at 55.5–56°.

Our researches on thiocyanates and isothiocyanates will be continued.

Experimental Part.

Preparation of Thiophosgene, $CSCl_2$.—All of this reagent, which we used in this investigation, was prepared by reduction of perchloromethylmercaptan.[1] The chloride was twice distilled and the product used boiled at 72–76°. The yield of thiophosgene was 75% of the theoretical based upon the weight of perchloride taken for reduction.

Preparation of the Ethyl Ester of Alanine and Its Corresponding Hydrochloride.—The most practical method for preparing racemic alanine synthetically in quantity is by application of the synthesis developed by A. Strecker,[2] which is based on the interaction of aldehyde ammonia and hydrocyanic acid in hydrochloric acid solution. Several methods for applying the reaction have been proposed. Heintz,[3] who was the first investigator to use potassium cyanide as a source of the cyanogen in a reaction of this type, showed that the aldehyde ammonia and this salt interact smoothly in an aqueous solution of hydrochloric acid giving good yields of alanine. Ljubavin[4] later modified this procedure by substituting

[1] Johnson and Hemingway, THIS JOURNAL, 38, 1550 (1916).

[2] *Ann.*, **75**, 27 (1850).

[3] *Ibid.*, **169**, 120 (1873).

[4] *Zeit. Russ. Chim.*, **12**, 410 (1880); *Zentrbl.*, **1881**, p. 119.

ammonium cyanide in place of the potassium salt and showed that it interacted smoothly with acetaldehyde in hydrochloric acid solution with formation of the same aminoacid. In other words, the ammonium cyanide played a double role in furnishing both the ammonia and hydrocyanic acid. Later in 1906 Zelinsky and Stadnikoff[1] modified Ljubavin's procedure and showed that the nitrile of alanine results by interaction of potassium cyanide and ammonium chloride with acetaldehyde in aqueous or dilute alcohol solution. This development was continued by Zelinsky, Annenkoff and Kulikoff[2] in 1911. They investigated the reaction of molecular proportions of potassium cyanide and ammonium chloride in aqueous solution with acetaldehyde in ether, and operated as follows:

They added the cyanide solution slowly to a mixture containing the ammonium chloride in water and the aldehyde in ether. After allowing to stand for 40 hours and finally shaking violently for 5 hours they then subjected the aqueous solution to hydrolysis and isolated their alanine in the form of its ethylester. They obtained a yield of 20% of the theoretical. They later found that long standing was unnecessary and showed that by continual shaking and reducing the time of reaction to 15 hours the yield of ester could be raised to 40% of the calculated. The latest paper dealing with this method of synthesis is that contributed by Aschan and Vaskio.[3] They dissolved acetaldehyde in a cold aqueous solution of ammonia, then added slowly potassium cyanide in aqueous solution and finally with cooling a definite amount of conc. hydrochloric acid. After allowing such a mixture to stand for about 12–14 hours it was worked for alanine. The yield obtained is stated to be about 15.8% of the theoretical.

The source of the cyanide radicle in these applications of Strecker's synthesis has been potassium cyanide. Since this is now difficult to obtain it was thought advisable to determine whether the cheaper and readily obtainable commercial sodium cyanide mixture could be employed in its place. A direct comparison in behavior towards acetaldehyde was made experimentally by employing both salts under different but comparable conditions. First, pure aldehyde-ammonia was used; second, pure acetaldehyde was conducted into the cyanide solution to which was added an equivalent amount of ammonia and, third, the entire distillate of crude aldehyde containing alcohol was led directly into the cyanide solution containing ammonia. The acetaldehyde was prepared by oxidizing ethyl alcohol with sodium dichromate and sulfuric acid. In general, 1 kg. of 95% ethyl alcohol with 2 kg. of sodium dichromate, dissolved in 2 kg. of water, reacted with 1.1 kg. of conc. sulfuric acid dissolved in 2 kg. of water to give 305–310 g. of aldehyde-ammonia. The first experiment was con-

[1] *Ber.*, **39**, 1722 (1906).
[2] *Zeit. Physiol. Chem.*, **73**, 459 (1911).
[3] *Ber.*, **48**, 874 (1915).

ducted with potassium cyanide and was carried out under the following conditions:

Two hundred and fifty g. of acetaldehyde-ammonia was dissolved in a cold solution of 250 grams of ammonium chloride in 850 cc. of water; and then was added slowly, with cooling, a solution of 270 g. of potassium cyanide in 450 cc. of water. The resulting mixture was now allowed to warm to room temperature and finally to stand at ordinary temperature for 24 hours. The solution remained strongly alkaline. It was then acidified strongly with conc. hydrochloric acid, 400–500 cc. of which were required to produce an acid reaction; and the solution finally evaporated to dryness on a steam bath. During the concentration crops of potassium and ammonium chlorides were filtered off by suction and extracted with absolute alcohol to save any alanine hydrochloride present. The final thick, pasty residue of impure alanine hydrochloride was dried as completely as possible and then esterified in the usual way with absolute ethyl alcohol. In order to effect complete esterification the excess of alcohol was removed under diminished pressure and the operation repeated with fresh alcohol. To obtain the free ester of alanine Fischer's method of operating[1] was applied with the modification of salting out the ester with anhydrous sodium carbonate instead of the potassium salt. The method suggested by Zelinsky[2] was not applied. The yield of pure alanine ester obtained was 122 g. boiling at 54° at 17–18 mm. pressure.

In order to determine whether sodium cyanide could be substituted for the potassium salt this experiment was repeated with the following modification in procedure: *i. e.*, 275 g. of the commercial sodium salt, containing cyanide equivalent to that in 98% potassium cyanide, was dissolved in 750 cc. of cold water and substituted for the potassium cyanide. In all other respects, the conditions were the same as in the previous experiment. We obtained 130 g. of the alanine ester boiling at 49–54° at 11–12 mm. pressure. In other words, the yield of alanine was as good as when potassium cyanide was used to furnish the cyanide radicle.

We next conducted experiments to determine whether the amino acid synthesis might be applied successfully without first preparing acetaldehyde ammonia. Pure acetaldehyde gas was passed directly into an aqueous solution of potassium cyanide and ammonium chloride containing an equivalent amount of ammonia. We used 54 g. of potassium cyanide, 50 g. of ammonium chloride, 56 g. of concentrated ammonia solution and 250 cc. of water and an amount of alcohol necessary to produce acetaldehyde equivalent to 50 g. of aldehyde-ammonia. In other respects the operation was the same as before, and we obtained 20 g. of alanine ester boiling at 53–56° at 19–20 mm. and 47–49° at 13 mm. pressure. This experiment

[1] *Ber.*, **34**, 433 (1901).

[2] *Loc. cit.*

was repeated with substitution of 55.1 g. of commercial sodium cyanide in place of the 54 g. of potassium cyanide. We then obtained 30 g. of the amino acid ester boiling at 47–49° at 10–11 mm. and on redistillation at 48.5–50° at 9 mm. pressure.

Further experiments demonstrated that it was unncessary to purify at all the acetaldehyde for amino acid synthesis. The crude distillate from the oxidation of ethylalcohol was conducted directly into the aqueous solution of sodium cyanide, ammonium chloride and ammonia. Using the same proportions of reacting substances as were employed in the previous experiments and operating under similar conditions we obtained 29.4 g. of alanine ester boiling at 57–61° at 17–18 mm. pressure. In other words, as good a result was obtained as when pure acetaldehyde gas or the aldehyde-ammonia were used. This procedure furnishes a simple and convenient method for preparing alanine ester cheaply from readily obtainable material.

The Hydrochloride of the Ethyl Ester of Alanine.—The hydrochloride of inactive alanine ester was prepared by saturating a dry toluene solution of the amino acid ester with dry hydrogen chloride. It deposited in a crystalline condition and was purified further by crystallization from alcohol. It separated from this solvent as aggregates of hexagonal prisms which melted at 86.5–87° to a clean oil. If this salt is thoroughly dried until free from excess of hydrochloric acid it is not hygroscopic. This salt has previously been prepared by Curtius and Koch[1] from the amino acid by esterification, and after removal of the excess of alcohol to allow the salt to separate. They state that it deposited in the form of clusters of very hygroscopic needles which melted at 64–68°. The results of their analysis indicated that they were dealing with an impure product. They found 24.07% of chlorine, whereas the calculated value is 23.3%. Schmidt and Widman[2] prepared the same salt by passing hydrogen chloride into an ether solution of the ester. They assigned to it a melting point of 69–72°.

Action of Thiophosgene on Inactive Ethyl α-Aminopropionate. Ethyl Isothiocyanopropionate, $SCN.CH(CH_3).COOC_2H_5$.—This new isothiocyanate is formed smoothly by the action of three molecular proportions of the ester of alanine on one mole of thiophosgene, and is obtained as follows:

Seven and one-half g. of thiophosgene is dissolved in 100 cc. of anhydrous ether and 23 g. of the inactive alanine ester added slowly to the cooled solution. The reaction begins immediately and is strongly exothermal. Crystals of the hydrochloride of the aminoester separate almost immediately and the amount formed is practically quantitative, 19.5 g. being attained while theory calls for 19.8 g. This salt melted at 87°. After washing out

[1] *J. prakt. Chem.*, [2] **38**, 472 (1888).

[2] *Ber.*, **42**, 1886 (1909).

the dissolved hydrochloride of the amino acid ester and finally drying over anhydrous sodium sulfate, the ether is distilled off and the isothiocyanate then purified by distillation under reduced pressure. Eight grams of oil was obtained which boiled at 93.5° to 94.5° at 13 mm. pressure.

The density of the oil was determined by means of a pycnometer and the following values were obtained:

$$D_{40}^{20} = 1.0985 \text{ and } 1.0988$$
$$D_{40}^{20} = 1.1000 \text{ and } 1.1003$$

The index of refraction, which was measured with an Abbé refractometer was found to be as follows: $n_D^{20} = 1.4915$.

Analysis for sulfur (Carius):
0.2057 g. subst. gave 0.2056 g. $BaSO_4$.
Calc. for $C_6H_9O_2NS$: S, 20.15. Found: 20.4.

In one experiment, 4, molecular proportions of the amino acid ester and one equivalent of thiophosgene were taken with the idea of obtaining the corresponding thiourea according to the following equation:

$$CSCl_2 + 2NH_2CH(CH_3)COOC_2H_5 = CS(NHCH(CH_3)COOC_2H_5) + 2HCl.NH_2CH(CH_3)COOC_2H_5$$

Twenty grams of the inactive ester was taken and the operation carried on as in the previous experiment. Thirteen and seven-tenths g. of the hydrochloride of alanine ester separated from the ether while the theoretical yield for one-half conversion to the salt is 13.1 g. The ether solution was washed as usual, dried and the ether finally evaporated, when a dark red oil was obtained which was subjected to distillation in a vacuum. With the oil bath at 160–170° a light yellow oil distilled over at 92.5–93° at 12 mm. and 94–98° at 14 mm. pressure, but during this time there was continuous decomposition and this increased as the temperature was raised. The residue left behind was very dark colored and showed no signs of solidifying. It dissolved in ether at once, but when the ether was allowed to evaporate there was no deposit of crystalline material and only a gummy product was obtained. The oil which distilled over during the decomposition was identified as the mustard oil. The weight was about 2–3 g.

Action of Thiophosgene on the Hydrochloride of Inactive Ethyl α-Aminopropionate.—Twenty-six and three-tenths g. of the hydrochloride was suspended in 100 cc. of dry toluene and 24.6 g. of thiophosgene added during the course of 8 hours. The toluene was heated to 100–110° during this addition of thiophosgene and afterwards for a period of 12 hours. The hydrochloride melted in the toluene and separated as a layer of oil on the bottom of the flask. The mixture was heated until the evolution of hydrochloric acid practically ceased when the toluene layer was removed and the excess of thiophosgene and toluene expelled by distillation. The isothiocyanate was obtained as a dark red oil, which was purified by distillation under diminished pressure. The yield of purified prod-

uct was 10 g. and it boiled at 120.5–123° at 38–39 mm. pressure. This yield corresponds to only 37% of the theoretical. From the oily residue left in the flask we obtained, after making alkaline and extracting with ether, 5.5 g. of alanine ester boiling at 55–56° at 18 mm. pressure.

The refractive index of the mustard oil was found to be $n_D^{20} = 1.4935$ while the determination of density gave the values $d_4^{20} = 1.1060$ and $d_{20}^{20} = 1.1078$.

A sample, which was redistilled and boiled constant at 106.5° at 16 mm. pressure was analyzed for sulfur according to the method of Carius.

0.1518 g. subst. gave 0.2247 g. $BaSO_4$.
Calc. for $C_6H_9O_2NS$: S, 20.15. Found: 20.33.

In a second experiment 163.9 g. of the hydrochloride of ethyl α-amino propionate was taken for reaction and the operation applied as before. We obtained here only 18 g. of the aliphatic isothiocyanate boiling from 102–107° at 16–17 mm. pressure. The residue of oily hydrochloride was very large in this case and on working for ester we recovered 50 g. boiling at 52–53° at 11–13 mm. pressure. The yield of isothiocyanate based upon the amount of ester lost in reaction was only 18% of theory.

Action of Thiophosgene on the Hydrochloride of *d*-Ethyl α-Amino-propionate. The Formation of Dextro-Ethyl Isothiocyanopropionate, (α) $SCN.CH(CH_3)COOC_2H_5$.—The ester hydrochloride used here was prepared by esterification of *d*-alanine which was imported from Kahlbaum in Germany. Twenty-six and three-tenths g. of the *dextro* salt was subjected to the action of thiophosgene under similar conditions as described in the previous experiments and the resulting isothiocyanate purified by distillation. We obtained 11.5 g. of a light red oil which boiled at 100–101° at 11–12 mm. pressure. This corresponds to a yield of 42% of the theoretical.

In a second experiment we used the hydrochloride prepared from active alanine which was obtained by hydrolysis of silk.[1] From 84 g. of this active salt we obtained 25.5 g. of the mustard oil boiling at 107–109° at 12–14 mm. pressure. This yield was poorer, corresponding to about 29% of the theoretical. In a third experiment we used 66 g. of active hydrochloride and obtained 29 g. of the isothiocyanate boiling at 106–108° at 16–17 mm. pressure. This is a yield of 42% of the theoretical.

A determination of the index of refraction gave the following result:

$$n_D^{20} = 1.4935$$

Specific rotation of the isothiocyanate: A benzene solution containing 2.0663 g. of mustard oil in 100 cc. rotated at 20° in 2- and 4-decimeter tubes 1.23° and 2.46° to the right; hence $\alpha_D^{20} = +29.77$. These readings were made with a Schmidt and Haensch Triple Field Saccharimeter and converted to polariscope degrees by multiplying by the factor 34657. This sample of ester used for these measurements was allowed to stand in a stoppered bottle for six months and then redistilled. It boiled

[1] The silk was supplied by Cheney Brothers, Silk Manufacturers, South Manchester, Conn.

at practically the same temperature as before indicating no decomposition. A determination of the specific rotation was then made with the following result: 2.3783 g. of the oil in 100 cc. of benzene rotated at 20° in 2- and 4-decimeter tubes 1.525° and 3.084° to the right, hence $\alpha_D^{20} = +31.67$ and $+32.07$ or the average specific rotation of $+32.07$.

The refractive index of this particular sample was $n_D^{20} = 1.4925$.

Another measurement of rotation was made using a different sample when we found the following result:

2.1311 g. in 100 cc. of benzene at 20° gave in 2- and 4-decimeter tubes dextro rotations of 1.178° and 2.357°, respectively. Therefore $\alpha_D^{20} = +27.65$. Refractive index (Abbé) $n_D^{20} = 1.4945$.

Sulfur determination (Carius):
0.1501 g. subst. gave 0.2196 g. $BaSO_4$.
Calc. for $C_6H_9O_2NS$: S, 20.15. Found: 20.09.

Action of Aniline on Inactive Ethyl Isothiocyanopropionate. Formation of Ethyl Phenylmethyl-2-thiohydantoate, $C_6H_5NH.CS.NH.CH(CH_3).COOC_2H_5$.—The isothiocyanate displayed its constitution by its reaction with aniline. Two and nine-tenths g. of aniline in 2 cc. of ether was slowly added to a cold solution of 5 g. of the mustard oil in 50 cc. of ether. The solution assumed a light yellow color and much heat was evolved. After standing for 24 hours the ether was evaporated in a current of air when rosets of colorless crystals deposited. These were recrystallized from alcohol and melted at 83–84° to a clear oil. This ester is very soluble in alcohol, benzene and ether but unsoluble in water. The yield was practically quantitative. Nitrogen determination:

Calc. for $C_{12}H_{16}O_2N_2S$: N, 11.08. Found: 11.01, 10.96.

This experiment was repeated by applying the reaction without a solvent. One and two-tenths g. of aniline was mixed with 2 g. of the isothiocyanate when there was an immediate reaction with formation of a thick oil. This finally solidified and when recrystallized from alcohol melted at 83–84° to a clear oil. This same ester is also formed by allowing phenyl mustard oil to interact with inactive ethyl α-aminopropionate in ether solution. By evaporation of ether it was obtained in a crystalline condition and melted after crystallization from alcohol at 83–84°.

Action of Phenylisothiocyanate on Inactive Ethyl α-Aminopropionate. Formation of 1-Phenyl-4-methyl-2-thiohydantoin, $C_6H_5N.CS.NHCH(CH_3)CO$.—While ethyl isothiocyanopropionate and aniline interact, without use of solvents, to form the hydantoate combination, an entirely different result is obtained if the reaction is reversed and phenylisothiocyanate added directly to the ester of the amino acid. Eleven and five-tenths g. of the mustard oil was added slowly to 10 g. of alanine ester well cooled in ice water. There was an immediate reaction on mixing with evolution of much heat and a thick, yellow oil was obtained. This was allowed to stand

at room temperature when, after 2 hours, crystals began to deposit and within a few hours the whole mass had completely solidified. The product crystallized from hot alcohol and separated on cooling in the form of aggregates of distorted prisms. The yield was nearly quantitative. The hydantoin melted at 183.5–184.5° to clear oil. This hydantoin has been described by Aschan[1] who assigned to it a melting point of 184°.

Nitrogen determination: Calc. for $C_{10}H_{10}ON_2S$: N, 13.59. Found: 13.50.

Action of Phenylisothiocyanate on Dextro-Ethyl α-Aminopropionate.—Nine and two-tenths g. of phenylisothiocyanate was added to an ether solution containing 8 g. of the above ester. There was an immediate reaction with evolution of heat. This was allowed to stand for several hours and the ether then removed in the usual manner. We obtained a thick, viscous oil which showed no signs of crystallizing. In fact, this product remained as an oil after standing in a desiccator for several weeks. We met with a similar experience when we reversed the reaction and allowed aniline to interact with ethyl isothiocyanopropionate in benzene solution. After heating the benzene solution for 2 hours and then removing the solvent we obtained an oil which showed no signs of solidifying on cooling. It remained in this form for 6 months without showing any signs of depositing crystals.

Formation of Thionurethane, $C_2H_5OOC.CH(CH_3)NH.CSOC_2H_5$ by Interaction of Ethyl Alcohol with Ethyl Isothiocyanopropionate.—Five grams of ethyl isothiocyanopropionate was dissolved in 20 g. of absolute alcohol and the solution then heated on the steam bath for about 3 hours. The alcohol was then removed by distillation when the methane was obtained as a viscous oil. We obtained 5.5 g. of this substance which distilled as a yellow oil boiling at 157–159° at 18–19 mm. pressure. On standing at room temperature this oil finally crystallized and on recrystallization from ether or ligroin separated in the form of slender prisms which melted at 55.5–56°. The yield corresponded to 85% of the theoretical.

Calc. for $C_8H_{15}O_3NH$: N, 6.85. Found: 6.83.

The Action of Thiophosgene on Alanine.—All our attempts to prepare isothiocyanopropionic acid by the action of thiophosgene on the amino acid alanine were unsuccessful. The amino acid and thiophosgene were digested together in dry toluene, and the reaction also applied by heating the acid with thiophosgene without solvents, in sealed tubes at 100°, 130°, 140° and 150°, but in no case did we succeed in obtaining a smooth reaction. Much of the alanine was recovered and amorphous or charred products were formed from which it was impossible to isolate definite compounds.

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[1] *Ber.*, 16, 1544 (1883).